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ENVIRO
Technical
Information for
Problem
Spills

SODIUM HYDROXIDE

June 1984

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

SODIUM HYDROXIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

SODIUM HYDROXIDE (NaOH)

White solid, flakes or powder; clear aqueous solution with no odour

SYNONYMS

Caustic Soda, Lye, Sodium Hydrate, Soda Lye, White Caustic, Hydroxyde de Sodium (Fr.), Sodium (Hydroxyde de) (Fr.)

IDENTIFICATION NUMBERS

UN No. 1823 (solid), 1824 (solution); CAS No. 1310-73-2; STCC No. 4935235 (dry), 4935240 (liquid), 4935243 (52 percent solution)

GRADES & PURITIES

Rayon and Regular Grades

Aqueous Solutions: 50 and 73 percent nominal concentrations

Anhydrous: 98.5 percent minimum (purity varies from supplier to supplier, generally from 96 to 99 percent minimum)

IMMEDIATE CONCERNS

Fire: Noncombustible. Anhydrous form in contact with water may generate sufficient heat to ignite combustible materials

Human Health: Corrosive to all tissues upon contact

Environment: Harmful to aquatic life in high concentrations

PHYSICAL PROPERTY DATA

	Anhydrous	50% solution	73% solution
State (15°C, 1 atm):	solid	liquid	liquid
Boiling Point:	1,390°C	140 to 145°C	188 to 193°C
Melting Point (Freezing Point):	318°C	12-13°C	62-63°C
Flammability:	noncombustible	noncombustible	noncombustible
Density:	2.130 g/cm^3 (20°C)	1.529 g/cm^3 (15.6°C)	1.730 g/cm^3 (70°C)
Solubility:	109 g/100 mL @ 20°C		
Odour Threshold:	no odour	no odour	no odour
Behaviour (in water):	sinks, dissolves and mixes, liberating heat		

ENVIRONMENTAL CONCERNS

The damaging effect of sodium hydroxide appears to be mostly a consequence of pH. The upper pH limit tolerated by most freshwater fish is 8.4.

HUMAN HEALTH

IDLH: 200 mg/m^3 (dust or mist)

Exposure Effects

Inhalation: Dust or mist can cause injury to the respiratory tract

Contact: Severe burns can be produced on all human tissue from contact with solid or liquid forms. Multiple small burns may result from exposure to dust or mist. Eye contact can produce severe or permanent injury

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid skin contact and inhalation of dust and mist. Keep contaminated water from entering sewers or watercourses.

Fire Control

Noncombustible.

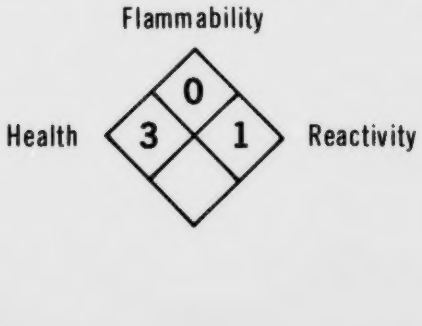
COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable surfaces. Solid: Promptly shovel up into steel containers. Liquid: Absorb small amounts of spill with sand, vermiculite or other inert absorbant material; shovel into steel containers. One may also remove material with vacuum equipment

Water: Contain discharge by damming or water diversion. Dredge or vacuum pump to remove contaminated bottom sediment. Sodium dihydrogen phosphate may be used as an *in situ* neutralizing agent

NFPA HAZARD CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties	Anhydrous	50% Solution	73% Solution
Appearance	White, translucent crystalline solid (Kirk-Othmer 1978)	Clear to white	Clear to white
Usual shipping state(s)	Solid	Liquid	Liquid (at elevated temperature)
Physical state at 15°C, 1 atm	Solid (Kirk-Othmer 1978)	Liquid (Hooker PIM)	Solid (Hooker PIM)
Melting point	318°C (CRC 1980; Kirk-Othmer 1978)	11°C (Hooker PIM)	62°C (Hooker PIM)
Freezing point		12-13°C (Kirk-Othmer 1978)	62-63°C (Kirk-Othmer 1978)
Boiling point	1,390°C (CRC 1980; Kirk-Othmer 1978)	140 to 145°C (Dow MSDS 1979; GE 1978; Dow 1980)	188 to 193°C (Dow 1980)
Densities			
Density	2.130 g/cm^3 (20°C) (Roznjevic 1976)	1.529 g/cm^3 (15.6°C) (Kirk-Othmer 1978)	
Specific gravity (water=1)	2.130 (20°C) (CRC 1980; Dow 1980; Kirk-Othmer 1978)	1.530 (20°C/4°C) (Merck 1976) (15.6°C) (Dow 1980)	1.730 (70°C) (Dow 1980)
Bulk density:	Crystal, 709.6 kg/m^3 Flake, 1,001.2 kg/m^3 Powder, 662.7 kg/m^3 (Chemtech)		

Fire Properties

Flammability	Noncombustible; on contact with water, may generate sufficient heat to ignite combustible materials (NFPA 1978). Will not support combustion (Kirk-Othmer 1978)
Decomposition products	Thermodynamically stable. Vaporizes at 1,390°C at 1 atm without decomposition (Eblin 1968; Bailar 1973)
Behaviour in a fire	Reaction with amphoteric metals such as aluminum, tin and zinc causes hydrogen generation which may form an explosive mixture (Kirk-Othmer 1978)

Other Properties	Anhydrous	50% Solution	73% Solution
Molecular weight of pure substance	39.998 (Kirk-Othmer 1978)		
Constituent components (%) (of typical commercial grades)	> 96 percent NaOH, 96.4 percent NaOH (typical)	50 percent anhydrous NaOH, 50 percent H_2O	73 percent anhydrous NaOH, 27 percent H_2O
Refractive index	1.3576 (CRC 1980; Kirk-Othmer 1978)		
Viscosity	4 mPa•s (350°C) (GE 1978; Dow 1980)	73 mPa•s (21.1°C) (Hooker PIM)	27 mPa•s (65.6°C) (Hooker PIM)
Hygroscopicity	Rapidly absorbs carbon dioxide and water from air (Merck 1976)		
Latent heat of fusion	167.4 kJ/kg (Kirk-Othmer 1978)		
Heat of formation	426.3 kJ/mole (JANAF 1971) α:10 562 kJ/kg β:10 565 kJ/kg (Kirk-Othmer 1978) gas :5 181 kJ/kg (CRC 1983)		
Heat of vaporization	3 307.572 kJ/kg @ 101 kPa (Roznjevic 1976)	-469.6 kJ/mole (CRC 1980)	
Heat of solution	-1 113.4 kJ/kg @ 25°C (CRC 1983)	-535.7 kJ/kg @ 25°C ($NaOH \cdot H_2O$) (CRC 1983)	
Heat of transition ($\alpha \rightarrow \beta$)	103.3 kJ/kg (Kirk-Othmer 1978)		
Transition point ($\alpha \rightarrow \beta$)	299.6°C (Kirk-Othmer 1978)		
Lattice energy	22,176 kJ/kg (CRC 1983)		
Heat of crystallization	$NaOH \cdot H_2O$: 1 310 kJ/kg (Dow 1980) $NaOH \cdot 3.5\ H_2O$: 582 kJ/kg (Dow 1980)		
Coefficient of cubical expansion	(Solid) 0.000084 (l/k) (20°C) (Roznjevic 1976)		
Thermal conductivity		0.710 W/(m•K) (76.7°C) (Hooker PIM)	0.720 W/(m•K) (Hooker PIM)

	Anhydrous	50% Solution	73% Solution
Electrical conductivity	0.0212 ohm^{-1} m^{-1} (Molten at 320°C) (Dow 1980)		
Heat capacity constant pressure (C_p)	59.53 J/(mole•°C) (JANAF 1971)	3.203 kJ/(kg•K) (Hooker PIM)	2.676 kJ/(kg•K) (Hooker PIM)
pH of aqueous solution		14 (5 wt. % solution) (Merck 1976) 13 (0.5 wt. % solution) (Merck 1976) 12 (0.05 wt. % solution) (Merck 1976)	

Solubility

In water	42 g/100 mL (0°C) (Hooker PIM) 109 g/100 mL (20°C) (Hooker PIM) 347 g/100 mL (100°C) (Hooker PIM)
In other common materials	soluble in glycerol (Merck 1976; CRC 1982) Insoluble in acetone and in diethyl ether (CRC 1980) Methanol: 30.8 g/100 g MeOH @ 28°C (Bailar 1973) Ethanol: 7.2 g/100 g ETOH @ 28°C (Bailar 1973)

General Summary

Due to the electropositive nature of the alkali metals, their hydroxides are the most basic of all hydroxides. Within the Group 1A hydroxides, the basic strength increases with increasing cation size; sodium hydroxide is thus the weakest of the stable hydroxides (NaOH<KOH<RbOH<CsOH). These four compounds are very stable in that they retain hydrogen without the loss of water well past their melting points. They volatilize as the hydroxides, rather than first dehydrating (such as LiOH) and then volatilize as the oxide. They can be sublimed unchanged at 350-400°C; the vapours consist mainly of dimers $(MOH)_2$. Their boiling points decrease with increasing atomic weight of the metal. In general, their thermal stability is roughly proportional to their basicity (thermal stability increases with atomic weight of the metal) (Bailar 1973; Cotton 1972).

Pure, anhydrous sodium hydroxide is a white, translucent crystalline solid. It is highly deliquescent and will absorb moisture and carbon dioxide from the air, resulting in the formation of sodium carbonate (Na_2CO_3). It is readily soluble in water, forming a colourless solution the viscosity of which increases greatly with concentration. The solution is highly alkaline and even in moderate concentrations is very corrosive (Kirk-Othmer 1978).

In water solution, depending on concentration, sodium hydroxide can form six hydrates containing 1, 2, 3.5, 4, 5 and 7 molecules of water, respectively. Hydrate formation is exothermic; as such, sodium hydroxide solutions evolve heat when further diluted with water. This is readily depicted by the following table showing the dilution temperatures of anhydrous sodium hydroxide, and of 73 percent solution to 50 percent solution (Kirk-Othmer 1978; Bailar 1973):

Dilution Temperature of Anhydrous[a] NaOH (Dow 1980)

Initial Temp. of Water (°C)	Resultant Temperature (°C) of	
	50% Sol'n	73% Sol'n
4	100	61.1
16	107.2	65.6
27	113.9	68.3
38	121.7	71.1
b.p.	144.7	-

[a] Based on flake or solid NaOH at 24°C

Dilution of 73% Solution to 50% Solution (NaOH) (Hooker PIM)

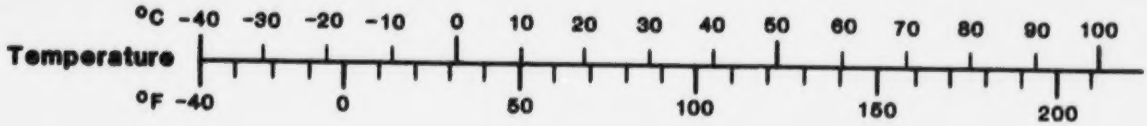
	Initial Temp. of 73% Solution (°C)				
	82.2	87.8	93.3	98.9	104.4
Temp. of Added Water (°C)	Resultant Temperature of 50% Solution (°C)				
4.4	112.8	115.6	118.9	121.7	125
10	115	117.8	120.6	123.3	126.7
15.6	117.2	120	122.8	125.6	128.9
21.1	119.4	122.2	125	127.8	130.6
26.7	121.7	124.4	127.2	130	132.8

The heat generated from the dissolution of solid sodium hydroxide or the dilution of solutions can raise the temperature of the liquid above the boiling point of the solution and result in severe bumping. Adding water to a large volume of 73 percent sodium hydroxide solution causes a violent eruption (Kirk-Othmer 1978).

Even though sodium hydroxide is produced and shipped in the anhydrous state in various forms, very little is actually used as such. It is used almost exclusively in water solutions of less than 50 percent concentration. The 73 percent solution, which can be an economical form for very large users, is usually diluted and cooled before storing. Dilution eliminates the need for nickel handling and storage equipment and also lowers the freezing point of the solution. The latter reduces the amount of steam required for heating storage tanks and transfer lines. As a point of reference, dilution of 37.85 m^3 of 73 percent sodium hydroxide solution requires about 29.53 m^3 of water and produces about 61.32 m^3 of 50 percent solution. Since a considerable rise in temperature occurs during dilution, the resultant 50 percent solution must be cooled to about 40°C or lower to reduce its corrosive effect on iron and steel storage and handling equipment. The specifics concerning dilution techniques are available from the manufacturers. Generally, the 50 percent solution is the most convenient and economical form to buy, even though the purchaser pays freight on the extra water. The handling facilities are much more expensive for 73 percent sodium hydroxide solutions (Kirk-Othmer 1978; Hooker PIM; Dow 1980). There is a relatively flat portion of the freezing point curve (65-74 percent) for sodium hydroxide; over this range of concentrations, the solution freezes at about 62°C. Nominal 73 percent solution remains in the liquid state at a temperature of 62°C and can be handled as a liquid as long as it is kept above this temperature. At concentrations above 74 percent, the temperature required to keep the solution in the liquid state rises sharply. The 50 percent solution remains liquid at room temperature (Kirk-Othmer 1978).

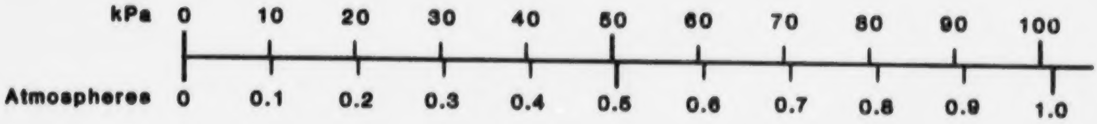
The chemical reactions of sodium hydroxide are those expected of a strong base. The aqueous solutions react with even very weak acids to form sodium salts. Sodium hydroxide reacts with alcohols to form the corresponding alkoxide, NaOR. It will neither burn nor support combustion, although its reaction with amphoteric metals such as aluminum, zinc and tin generates hydrogen gas which may form an explosive mixture with air. The reaction with metals forms soluble salts. The precipitation of metals as their hydroxides, e.g. $Mg(OH_2)$ from seawater, is becoming increasingly important for pollution control. Nearly complete metal removal can be accomplished by precipitation and settling, thereby providing an acceptable effluent for disposal. All organic acids react with sodium hydroxide to form soluble salts; organic esters react to form the corresponding salt and an alcohol (saponification). Sodium hydroxide is an important participant in many coupling reactions, such as the reaction with cellulose $(C_6H_{10}O_5)_n$ and monochloroacetic acid ($ClCH_2COOH$) to produce the sodium salt of carboxymethylcellulose. The first step in this reaction is similar to that used in the preparation of rayon by way of cellulose xanthate (Kirk-Othmer 1978; Bailar 1973).

CONVERSION NOMOGRAMS


Temperature
°C -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100
°F -40 0 50 100 150 200

Pressure

1 kPa = 1,000 Pa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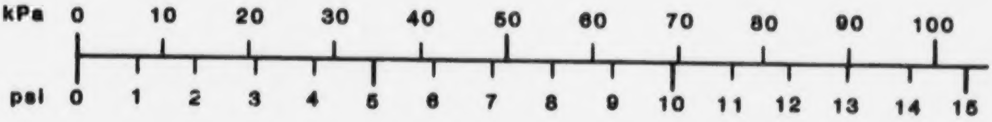
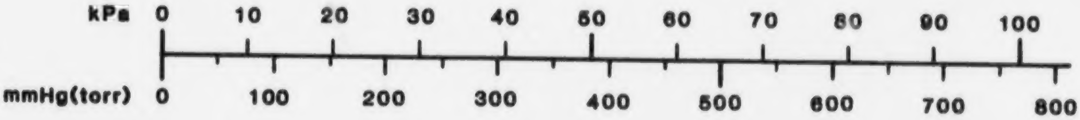
Atmospheres 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0


kPa 0 10 20 30 40 50 60 70 80 90 100
psi 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15


kPa 0 10 20 30 40 50 60 70 80 90 100
mmHg(torr) 0 100 200 300 400 500 600 700 800

Viscosity

Dynamic 1 Pa·s = 1,000 centipoise (cP)

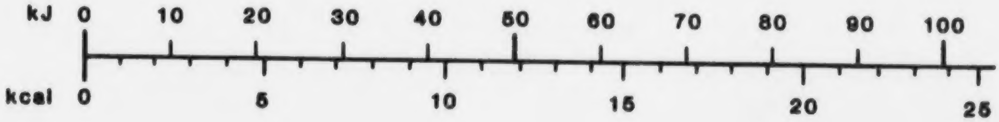
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

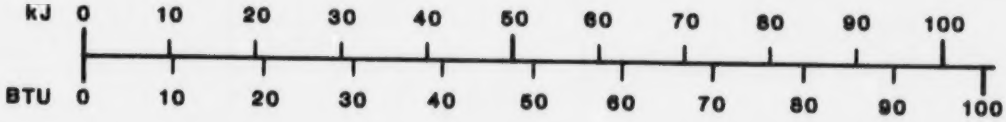
Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat)

1 kJ = 1,000 J


kJ 0 10 20 30 40 50 60 70 80 90 100
kcal 0 5 10 15 20 25


kJ 0 10 20 30 40 50 60 70 80 90 100
BTU 0 10 20 30 40 50 60 70 80 90 100

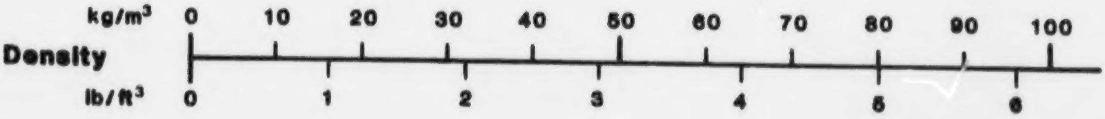

Density
kg/m³ 0 10 20 30 40 50 60 70 80 90 100
lb/ft³ 0 1 2 3 4 5 6

FIGURE 1

PHASE DIAGRAM OF NaOH/H_2O SYSTEM AND FREEZING POINT

Reference: DOW 1980, KIRK-OTHMER 1978, ULLMANN 1975

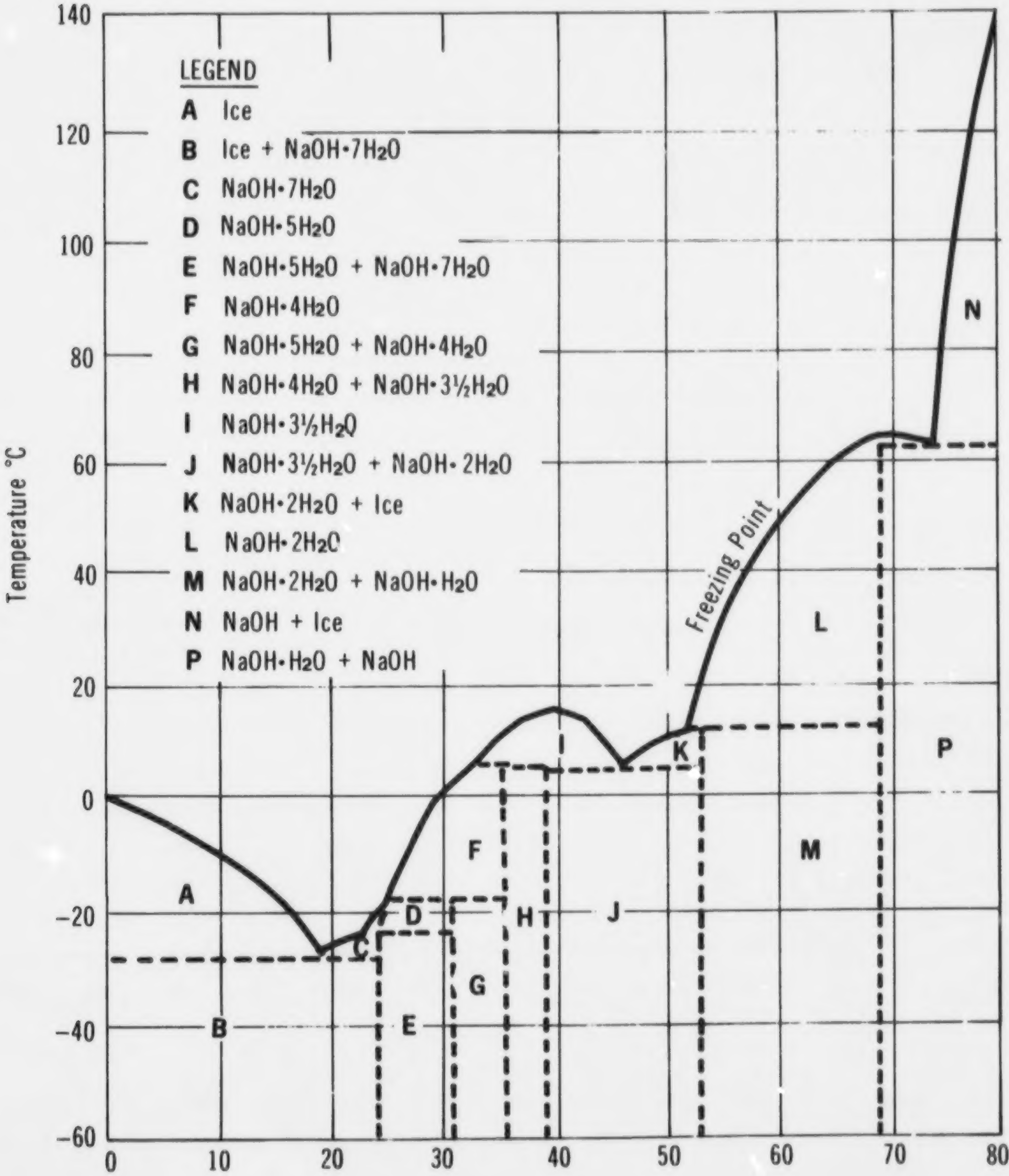


FIGURE 2

SODIUM HYDROXIDE

SPECIFIC GRAVITY OF SOLUTIONS

Reference: DOW 1980

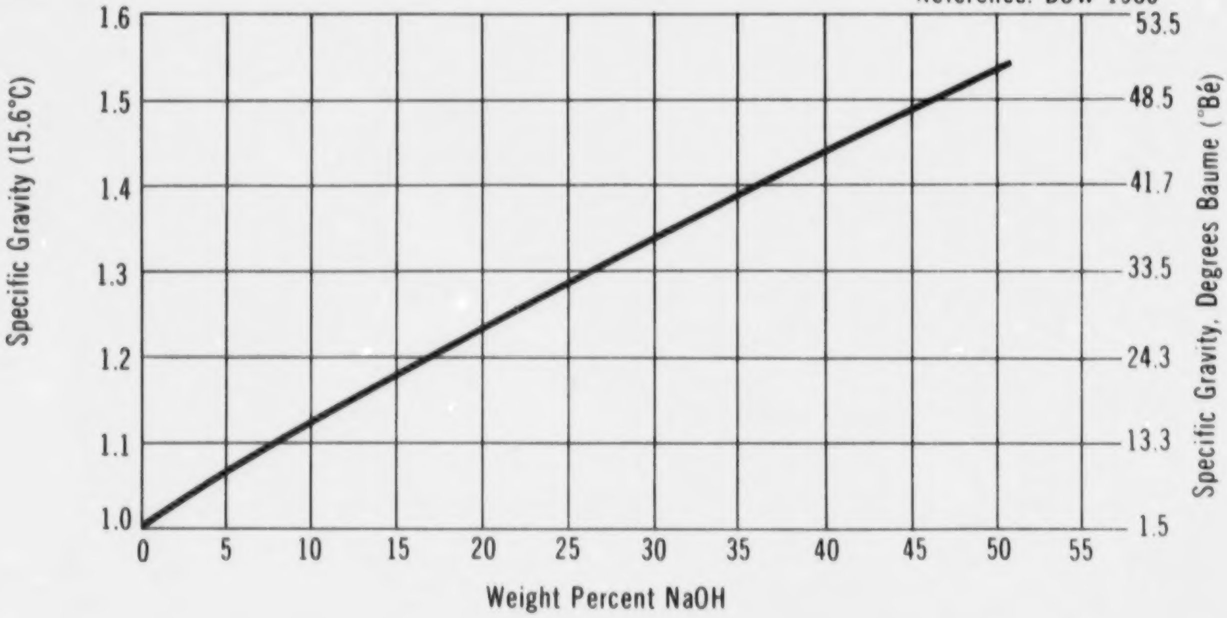


FIGURE 3

SODIUM HYDROXIDE

SOLUBILITY IN WATER

Reference: HOOKER PIM

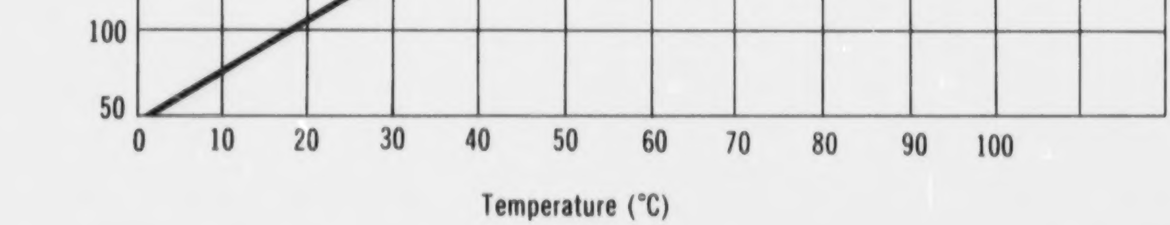


FIGURE 4

SODIUM HYDROXIDE

VAPOUR PRESSURE VS TEMPERATURE

Reference: HOOKER PIM

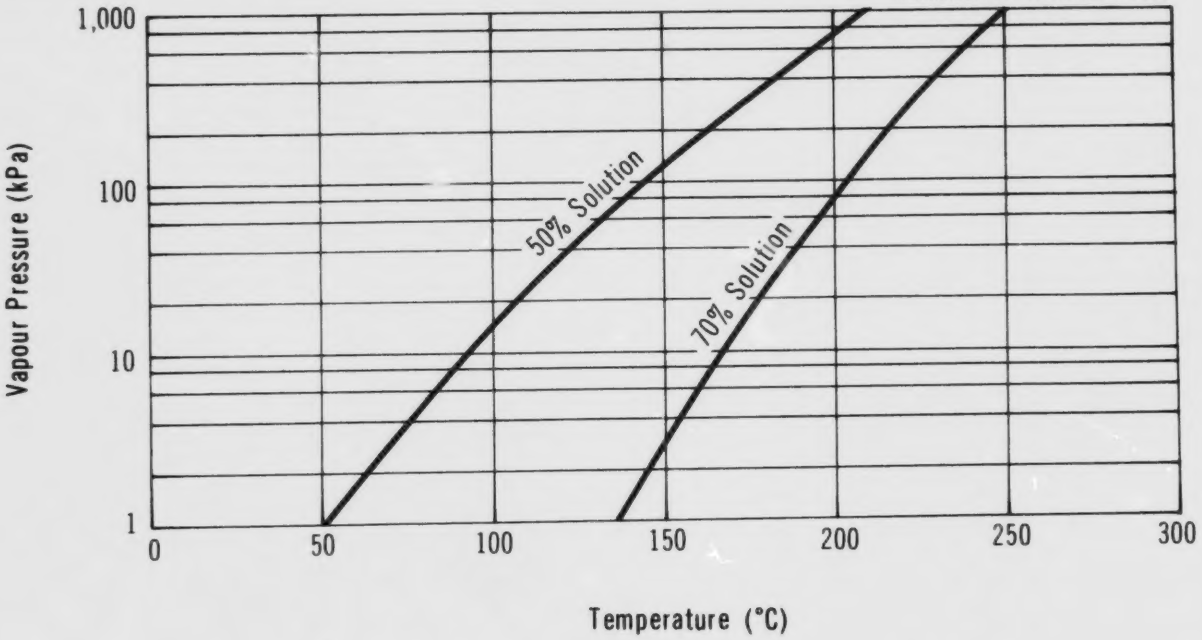
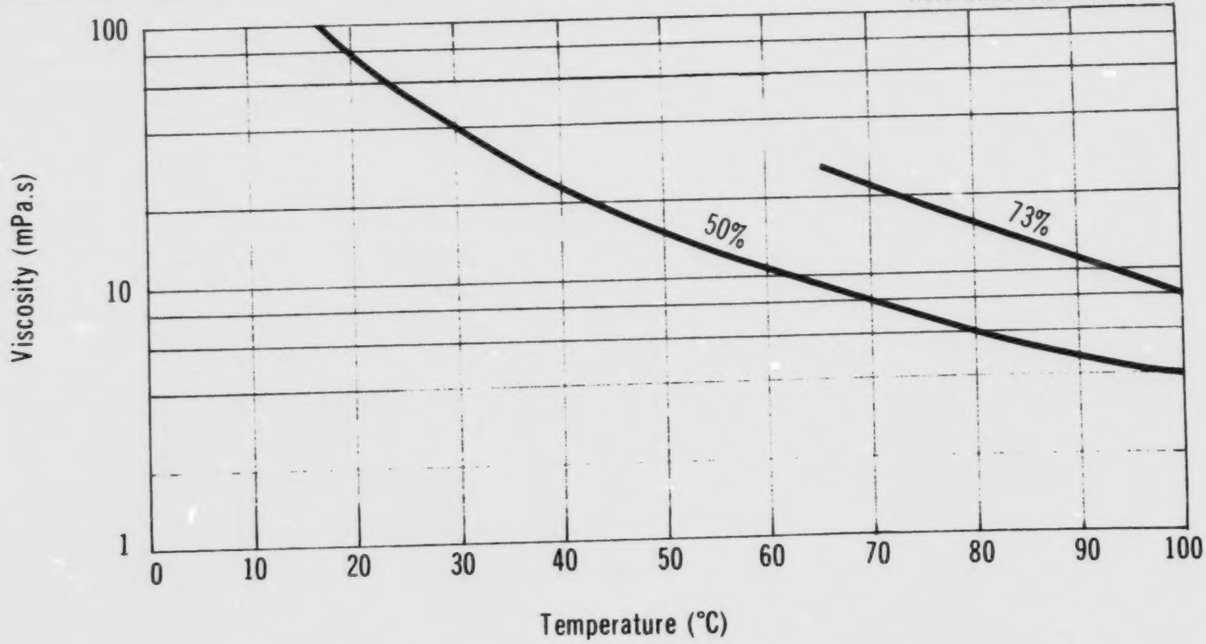


FIGURE 5

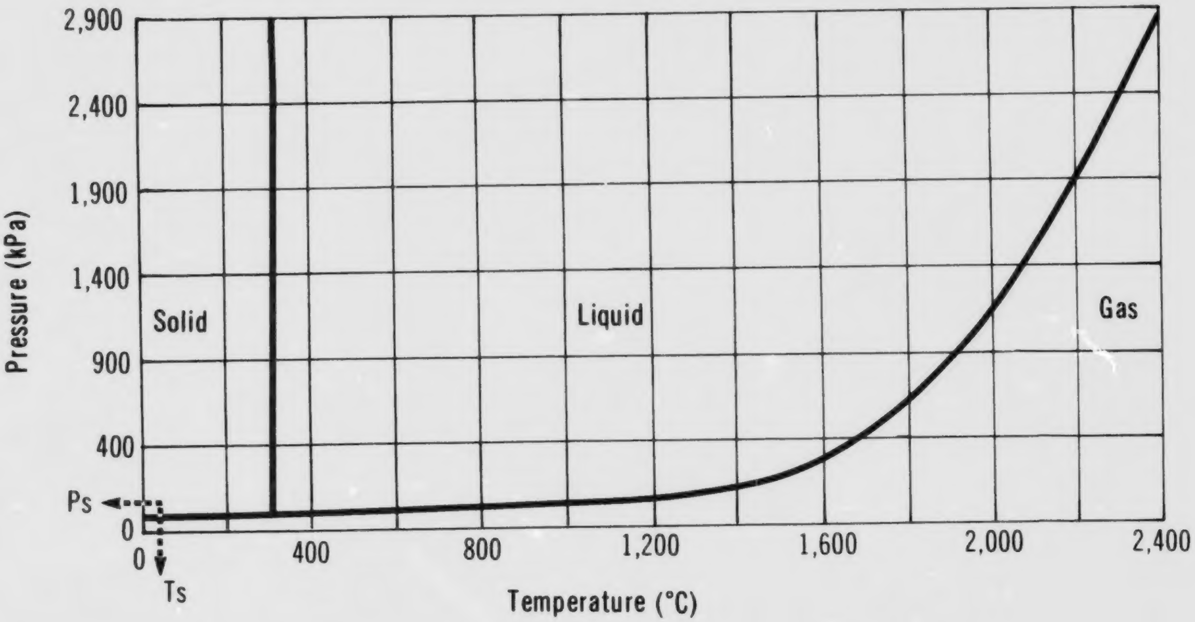
SODIUM HYDROXIDE

VISCOSITY VS TEMPERATURE

Reference: HOOKER PIM



PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

Sodium hydroxide is commonly sold in two commercial grades, rayon and regular, as an anhydrous solid, and in aqueous solutions of two concentrations, 50 and 73 percent. The anhydrous material is produced and shipped in the solid, flake or ground form. "Rayon grade" differs from "regular grade" in metal and chloride contents; otherwise the products are similar. The concentrations and their transportation forms are tabulated below (CIL MDS; Chemfacts Canada 1982).

Concentration	Form	Container
Anhydrous (98.5 percent minimum)	flakes, beads, pellets, powder	45 to 250 kg steel drums, fibre drums, 22.7 kg polyethylene bags
70 to 73 percent solution	liquid above 62°C	railway tank cars, tank motor vehicles
50 percent solution (49.0 percent minimum, 51.0 percent maximum)	liquid above 13°C	railway tank cars and tank motor vehicles

3.2 Domestic Manufacturers (Corpus 1983; CBG 1980; CCPA 1981)

These are corporate headquarters addresses and are not intended as spill response contacts.

Canadian Occidental Petroleum
Limited
Hooker Chemical Division
700 Fourth Avenue S.W.
Calgary, Alberta
T2P 0K2
(403) 265-2390

C-I-L Inc.
45 Sheppard Avenue East
Willowdale, Ontario
M2N 5W9
(416) 226-6110

Canso Chemicals Limited
P.O. Box 484
New Glasgow, Nova Scotia
B2H 0K2
(902) 755-1785

Dow Chemical Canada, Inc.
P.O. Box 1012
Modeland Road
Sarnia, Ontario
N7T 7K7
(519) 339-3131

FMC Chemicals
570-885 Dunsmuir Street
Vancouver, B.C.
V6C 1N5
(604) 685-6508

Great Lakes Forest Products Ltd.
Duke Street
Dryden, Ontario
P8N 2Z9
(807) 223-2323

Prince Albert Pulp Company Ltd.
Saskatoon Chemicals Division
P.O. Box 1586
Saskatoon, Saskatchewan
S7K 3R3
(306) 652-9456

Stanchem
Division of PPG Industries Canada
Limited
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9
(514) 933-6721

St. Anne Chemical Co.
8 Prince Arthur Avenue
Toronto, Ontario
M5R 1A9
(416) 968-2900

3.3 **Other Suppliers/Distributors** (Corpus 1983; CBG 1980)

Bayer (Canada) Inc.
7600 TransCanada Highway
Pointe Claire, Quebec
H9R 1C8
(514) 697-5550

Diamond Shamrock Canada Limited
1685 Main Street West
P.O. Box 5123, Station E
Hamilton, Ontario
L8S 4L4
(416) 823-7550

International Minerals and
Chemical Corp. (Canada) Ltd.
Box 310
Esterhazy, Saskatchewan
S0A 0X0
(306) 745-3931

Kingsley and Keith
19 Four Seasons Place
P.O. Box 555
Etobicoke, Ontario
M9C 5B1
(416) 626-8383

Pennwalt of Canada Limited
700 Third Line
Oakville, Ontario
L6J 5A3
(416) 827-8986
961-6500

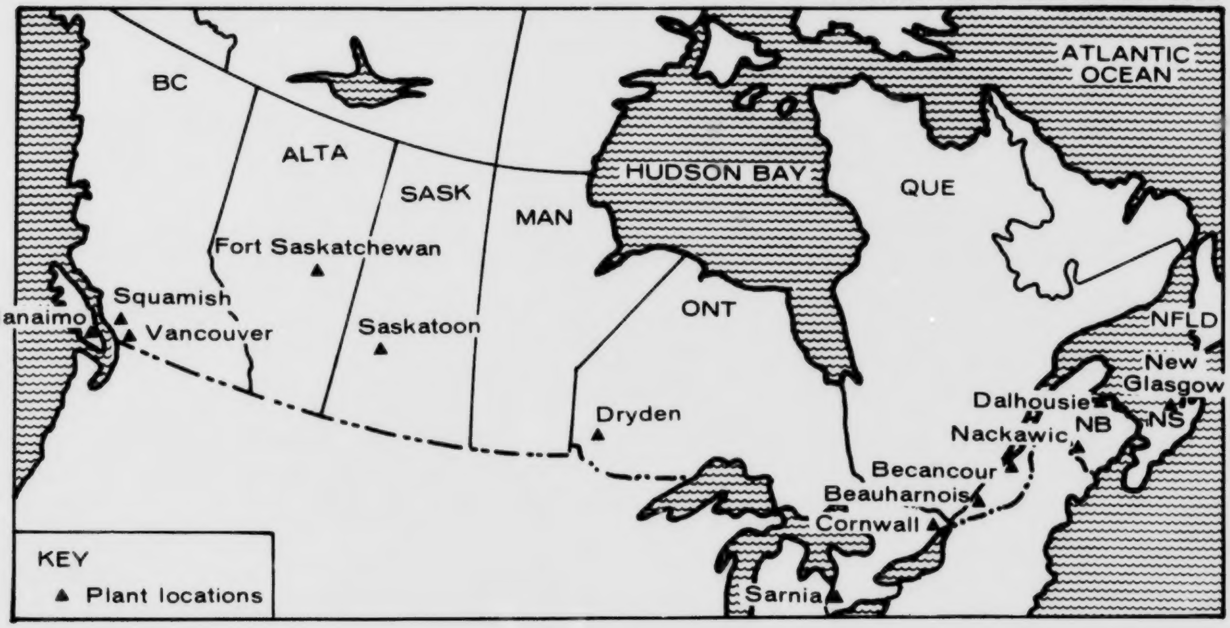
3.4 Major Transportation Routes

Current Canadian production of sodium hydroxide is very widespread, occurring in seven out of ten provinces. The largest production facilities are near Montreal and Quebec City, Quebec; Sarnia, Ontario; Fort Saskatchewan, Alberta; and in the lower B.C. mainland and on Victoria Island. A map showing plant locations is shown in Figure 7.

FIGURE 7

CANADIAN PRODUCERS

Reference: Chemfacts Canada 1982


BC
ALTA
SASK
MAN
HUDSON BAY
QUE
ATLANTIC OCEAN
ONT
NFLD
Fort Saskatchewan
Squamish
Nanaimo
Vancouver
Saskatoon
Dryden
New Glasgow
Dalhousie
NB
NS
Nackawic
Becancour
Beauharnois
Cornwall
Sarnia
KEY
▲ Plant locations

Sodium hydroxide solutions are shipped in railway tank cars and tank motor vehicles; the solid is transported in drums from the manufacturers to the users. Transportation is very widespread across Canada.

3.5 **Production Levels** (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
CIL, Becancour, Que.	325
CIL, Cornwall, Ont.	38.5
CIL, Dalhousie, N.B.	31
Canadian Occidental Petroleum, Vancouver, B.C.	155
Canadian Occidental Petroleum, Harmac, Nanaimo, B.C.	31
Canso Chemical, New Glasgow, N.S.	20
Dow Chemical Co., Sarnia, Ont.	350
Dow Chemical Co., Ft. Saskatchewan, Alta.	524
FMC Chemicals, Squamish, B.C.	75
Great Lakes Forest, Dryden, Ont.	16
Prince Albert Pulp, Saskatoon, Sask.	36
St. Anne Chemical, Nackawic, N.B.	10
Stanchem (PPG), Beauharnois, Que.	67
TOTAL	1 678.5

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
Domestic Production (1982)		1 367.4
Imports (1982)		172.7
	TOTAL SUPPLY	1 540.1

3.6 Manufacture of Sodium Hydroxide (Shreve 1977; Chemfacts Canada 1982; Savage 1979; Chemical Week 1981)

3.6.1 General. Sodium hydroxide is manufactured in Canada primarily by electrolysis of sodium chloride (brine). A co-product of this reaction is chlorine. For the most part, diaphragm or membrane cells are used; however, mercury cells may still be in limited use.

3.6.2 Raw Materials Occurrence and Extraction. Sodium chloride deposits occur in several geographic areas in Canada. The most extensively worked deposits are in Southern Ontario, from Goderich to Sarnia, Windsor and the Niagara area. At Goderich, deposits are mined by conventional underground excavation methods, as deposits are relatively shallow. In other areas, where deposits are deeper (610 m), salt is mined hydraulically by injecting water or recycled brine into the salt formations and bringing up saturated brine solution which is pumped to the manufacturing facilities. For smaller production facilities, such as paper mills, solid salt is usually brought in by rail and dumped into saturation tanks.

3.6.3 Raw Materials Processing. In general, the mercury and membrane cells have much in common in that they both require strong, pure brine. This can be made up by dissolving pure solid sodium chloride or incorporating a purification stage for the feed brine upstream of the cell. The membrane is prone to fouling by magnesium or calcium ions which are common in typical feed brine. Diaphragm cells, on the other hand, can run on dilute (20 percent) concentration and relatively impure brine, e.g., that produced by solution mining of salt deposits (Savage 1979).

3.6.4 Manufacturing Processes. Three types of electrolysis cells (membrane, diaphragm and mercury) are in use for the production of sodium hydroxide and its co-product, chlorine. It has been reported (Chemfacts Canada 1982) that mercury cells are in limited use (13 percent of annual capacity for 1982); industry predominantly uses the membrane and diaphragm cells. The advantages of a mercury cell are: a well-known technology, design improvements that reduce mercury losses to the environment, and a relatively pure product. Its disadvantages are: higher electrical power consumption, and its vulnerability to opposition from environmentalists. This latter aspect has led to the virtual retirement of this process (Chemical Week 1981), although as late as 1979 it was estimated that 50 percent of world chlor-alkali plants still used the mercury cell (Savage 1979).

Conceptually, the diaphragm process uses an asbestos diaphragm to separate the cell chambers; the membrane process uses ion-selective membranes. As reported in Chemical Week (1981), a new generation of electrolytic cells is under development that will hopefully reduce by more than 20 percent the energy consumed in the process. The basic aim is to boost cell efficiency through the use of new catalysts and partition membranes. In Canada, it was reported that Chemetics of Vancouver was developing a new membrane. Other companies were reported to be working with a new cathode that reduces hydrogen evolution (Diamond Shamrock - Chardon, OH); developing a hybrid cell that combines a new membrane with porous catalyzed electrodes (Occidental Research - Irvine, CA); studying a jumbo version of a cell that uses GE technology to bond the electrodes to the membrane surface (Oronzio de Nora Impiauti Eleltrochimici - Milan, Italy and Dow Chemical); and developing new membrane know-how (PPG Industries and Asahi Chemical Industry Co. and Asahi Glass Co. - Tokyo) (Chemical Week 1981). Even the mercury and diaphragm processes have undergone improvements. The introduction of closed-loop operation to enable better housekeeping of mercury or asbestos losses will no doubt have overcome some of the environmental objections associated with the use of the former. The emergence of energy-saving items such as metal anodes, improved diaphragm materials, and Raney nickel-coated cathodes should extend the life of diaphragm-cell units. It is reported that C-I-L of Becancour, Quebec, incorporated a 10 percent more energy-efficient ICI-Solvay design at their diaphragm-cell plant (Savage 1979; Chemical Week 1981).

Generally, the use of diaphragms permits the construction of compact cells with lower resistance primarily because the electrodes can be placed close together. Earlier versions allowed the sodium chloride solution to migrate through the pores of the diaphragm, resulting in substantial contamination of the sodium hydroxide produced at the cathode. Also, the caustic could back-migrate to the anode where it was electrolyzed to oxygen, thereby diluting the primary product (chlorine) and attacking the anode. As mentioned above, some work has been done to improve this process.

Ion-selective membrane research was undertaken to overcome these disadvantages. The new membranes permit the production of higher strength sodium hydroxide and reduce the requirement for investment in downstream cleanup processes. The membranes are typically prepared from fluorocarbons, e.g., perfluorosulphonic acid (Du pont) and perfluorocarboxylic acid (Asahi Chemical and Asahi Glass). Asahi has licensed the technology to Canada's St. Anne-Nackawic Pulp and Paper Co. (Nackawic, N.B.) and Prince Albert Pulp Co. (Saskatoon, Sask.). The most recent membrane designs reduce the consumption of electricity. Voltage efficiency is reduced because of the voltage drop across the cell (increases cell voltage required) which results from the physical spacing of electrodes and membrane. One developer (GE) has bonded the electrodes to the membrane through the use of a powdered conductive material of high catalytic activity. Catalytic performance is improved and electric current is more evenly distributed over the surface of the membrane resulting in, to date, an energy saving of 20 percent. Commercial sizes of this technology have been built, and further scale-up work has been started (Dow and de Nova) (Chemical Week 1981).

Occidental Research is developing a new hybrid system that uses the energy associated with the hydrogen by-product to purify and concentrate the sodium hydroxide by electrodialysis and to concurrently generate part of the d.c. electrical energy required by the chlorine cell. This process has the potential to reduce electricity purchases by 20 percent and the steam required for the evaporation of diaphragm-cell caustic by 75 percent. The ultimate goal is to reduce the energy consumed in making 1.128 tons (assumed to be metric) of sodium hydroxide and co-products to 1,750 kWh (6.3×10^9 J); a typical diaphragm cell uses about 2500 kWh (9.0×10^9 J). The cell is constructed of plastic, uses porous catalyzed electrodes, very narrow gaps, and a special cation-exchange dialysis membrane. The hybrid cell is different from a typical membrane cell in that it is free of chlorine and can use low-cost hydrocarbon-based membranes to achieve a caustic product with desirable purity and concentration. The system can be coupled directly to existing diaphragm cell circuits (Chemical Week 1981).

Typical diaphragm and membrane cells consist of two compartments separated by an absestos diaphragm (variations exist) for the former and a membrane for the latter. Chloride ions from the brine are oxidized at the anode (usually made from a proprietary formulation, e.g., graphite base) where they form nascent chlorine and ultimately chlorine gas. Sodium ions are reduced at the cathode (typically constructed of a steel wire grid) to metallic sodium, which immediately reacts with water to form sodium and hydroxide ions and hydrogen gas (Chemical Week 1981). The overall reaction is represented by the following equation:

$$2Na^+ + 2Cl^- + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2 \uparrow + Cl_2 \uparrow$$

It is imperative that the anode and cathode compartments be kept separate so that the chlorine will not react with the hydroxide and produce unwanted chlorates and hypochlorites (ClO_3^- and OCl^-). In the diaphragm cell, the diaphragm must therefore be porous enough to permit passage of the current-carrying chloride and hydroxide ions but not the molecular chlorine gas from the anode which would reduce the concentration of sodium hydroxide in the cathode compartment. Maximum efficiency is achieved in the diaphragm cell when the cathode liquor is removed (when containing about 10 percent sodium hydroxide and 15 percent sodium chloride) (Bailar 1973). In some complexes, this dilute caustic stream can be pumped to another production unit and used in its present form.

Concentration to the commercial 50 and 73 percent grades requires an evaporation process which will cause the sodium chloride to crystallize from the solution. This can be accomplished by multiple-effect evaporators and flash crystallizers (CIL MDS). Regular grade 50 percent sodium hydroxide solution from a diaphragm cell is suitable for most end uses. Higher purity caustic is required for rayon manufacture, the synthesis of alkyl aryl sulphonates, and the regeneration of anion exchange resins. Mercury-cell sodium hydroxide easily meets these requirements. The diaphragm-cell producers, however, have had to spend much time and effort on purification to compete for these high-purity markets. One such process used in the U.S. for many years is the ammonia extraction method. A two-phase system is formed by mixing anhydrous ammonia with the 50 percent caustic solution. The ammonia phase extracts salt (NaCl) and any sodium chlorate that may have formed together with some sodium hydroxide and water. The other phase contains about 62 percent sodium hydroxide and is essentially free of salt and chlorate but does contain some ammonia. This caustic phase is separated from the other and flash-distilled in a fractionating tower which recovers nearly anhydrous ammonia. The purified 62 percent solution can then be diluted to 50 percent or further evaporated to 73 percent or anhydrous grades (Kirk-Othmer 1978).

Sodium hydroxide solutions from Dow Chemical USA typically contain 2 percent sodium chloride (from normal diaphragm cell); however, they also offer purified solutions that contain slightly less than 0.2 percent, and a very high purity 50 percent solution that contains less than 50 ppm sodium chloride, with sodium chlorate approaching the limits of detection (Dow 1980).

3.6.5 Co-products/By-products. Co-products of the electrolysis of brine are chlorine and hydrogen. By-products may include sodium hypochlorite and sodium chlorate.

3.7 Major Uses in Canada (Corpus 1983)

Sodium hydroxide is used in the production of the following: pulp and paper, alumina, synthetic detergents, laundry bleach, sodium salts, xanthates, rayon, cellulose film, industrial cleaners, textile processing, uranium mining, petroleum refining, manufacture of other chemicals, surfactants, refining vegetable oils, and PF resins.

3.8 Major Buyers in Canada (Corpus 1983)

Abitibi-Price, Smooth Rock Falls, Iroquois Falls, Ont.; Beaupré, Kénogami, Que.
Admiral Sanitation, Toronto, Ont.
Alcan, Jonquière, Que.
Arliss Chemical, Montreal, Que.
Bartek Chemical, Burlington, Ont.
Bate Chemical, Toronto, Ont.
BC Forest Products, Crofton, Mackenzie, B.C.
BCL Canada, Cornwall, Ont.
Benson Chemical, Freelton, Ont.
Boise Cascade, Ft. Frances, Miramichi, Kenora, Ont.
Borden Chemical, Vancouver, B.C.; Toronto, Cobourg, North Bay, Brampton, Ont.
Bowaters Newfoundland, Corner Brook, Nfld.
Bristol Myers, Toronto, Belleville, Stratford, Ont.
Canada Colors & Chemical, Don Mills, Ont.
Canada Cellulose, Prince Rupert, Castlegar, B.C.
Canadian Forest Products, Pt. Mellon, B.C.
Canadian Hanson, Toronto, Ont.
Canadian International Paper, La Tuque, Matane, Trois-Rivières, Que.; Toronto, London, Hawkesbury, Ont.
Caribou Pulp, Quesnel, B.C.
Celanese Canada, Edmonton, Alta.
Colgate-Palmolive, Toronto, Ont.
Consolidated Bathurst, Pontiac, New Richmond, B.C.
Courtaulds, Cornwall, Ont.
Crestbrook Forest Products, Skookumchuck, B.C.
Cromac Chemical, Toronto, Ont.
Crown Forest Products, Campbell River, B.C.
Cyanamid Canada, Niagara Falls, Ont.
Denison Mines, Elliot Lake, Ont.
Diversey Wyandotte, Mississauga, Ont.
Domtar, Cornwall, Windsor, Ont.
Donohue, Clermont, St. Felicien, Que.
Dubois Chemical, Toronto, Ont.
Economies Lab, Toronto, Ont.

Eddy Forest Products, Espanola, Ont.
Erco Industries, Buckingham, Que.
Eurocan Industries, Kitimat, B.C.
Fraser, Atholville, N.B.
Gaspesia Pulp, Chandler, Que.
Great Lakes Forest, Thunder Bay, Ont.
Gulf Canada, Montreal East, Que; Mississauga, Toronto, Ont.
Harrisons & Crosfield, Toronto, Ont.
Hart Chemical, Guelph, Ont.
Imperial Oil, Sarnia, Ont.
Intercontinental Pulp, Prince George, B.C.
Irving Paper, Saint John, N.B.
James River Marathon, Marathon, Ont.
Kert Chemical, Toronto, Ont.
Kimberly-Clark of Canada, Terrace Bay, Ont.
Lake Utopia Paper, St. George, B.C.
Lever Detergents, Toronto, Ont.
M & T Chemicals, Hamilton, Ont.
MacMillan Bloedel, Harmac, Powell River, B.C.
Manfor, Le Pas, Man.
Myriad Detergents, Que.
Northwood Pulp, Prince George, B.C.
Ontario Paper, Thorold, Ont.
Papier Cascades, Cabano, Que.
Prince George Pulp and Paper, Prince George, B.C.
Proctor & Gamble, Hamilton, Ont.
Proctor & Gamble Cellulose, Grand Prairie, Alta.
Quebec North Shore, Baie Comeau, Que.
Rayonier Canada, Port Alice, Woodfibre, B.C.
Reichold, North Bay, Lindsay, Thunder Bay, Toronto, Ont.
Rio Algom Mines, Elliot Lake, Ont.
St. Anne Nackawic, Nackawic, N.B.
St. Regis Alberta, Hinton, Alta.
St. Raymond, Desbiens, Que.
Suncor, Ft. McMurray, Alta.
Syncrude Canada, Ft. McMurray, Alta.
Tahsis, Gold River, B.C.
Tembec Forest Products, Temiskaming, Que.
Thurso Pulp, Thurso, Que.
Uba Chemical, Mississauga, Ont.
Union Carbide Canada, Lindsay, Ont.
Van Waters & Rogers, Richmond, B.C.
Weyerhaeuser Canada, Kamloops, B.C.
Witco Chemical, Oakville, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Sodium hydroxide solutions are shipped bulk in specially designed railway tank cars, tank motor vehicles and portable tanks, and in drums and other special containers. Anhydrous or dry sodium hydroxide is shipped in bulk in hopper-type bulk vehicles or cars, pneumatic bulk cars or sift-proof tank cars, or in drums, usually in bulk solid, flake and, ground forms. It is also shipped in paper or plastic multiwall bags.

Sodium hydroxide may also be transported by marine vessel. Tankships used in the transportation of sodium hydroxide are constructed to standards specified in IMO (International Maritime Organization) publications entitled "The Recommendations Code of Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk" and "The International Bulk Chemical Code" under The Safety of Life at Sea (SOLAS) Convention 1974 and the International Conference on Marine Pollution (MARPOL) 1973/78. These codes were developed to provide an agreed international standard for the safe carriage of dangerous chemicals by prescribing the structural features of ships involved in such carriage and the equipment they should carry with regard to the nature of the products involved. Sodium hydroxide may be carried in a Type III ship which, by definition, "is designed to carry products of sufficient hazard to require a moderate degree of containment to increase survival capability in a damaged condition (CCPA 1983).

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of sodium hydroxide are classified under Class 103, 104, 105A and 111A tank specifications (CTC 1974). Table 2 describes each specification (TCM 1979).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
103W	Steel fusion-welded tank with dome. Uninsulated or insulated. Bottom outlet or washout optional.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (Cont'd)

CTC/DOT* Specification Number	Description
103AW	Steel fusion-welded tank with dome. Uninsulated or insulated. Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional.
103BW	Steel fusion-welded tank with dome. Uninsulated or insulated. Rubber-lined tank. Top unloading arrangement required. Bottom outlet or washout prohibited.
104W	Steel fusion-welded tank with dome. Insulated. Bottom outlet or washout optional.
105A100W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 690 kPa (100 psi).
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi)
111A60W2	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Test pressure 414 kPa (60 psi).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (Cont'd)

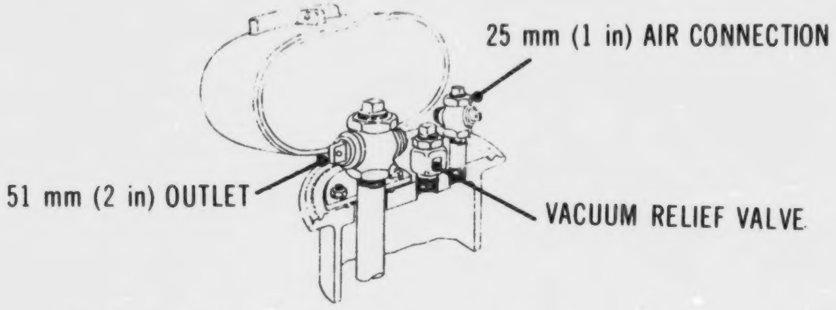
CTC/DOT* Specification Number	Description
111A60W5	Steel fusion-welded tank without dome. Uninsulated or insulated. Rubber-lined tank. 2% minimum outage. Gauging device. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 414 kPa (60 psi)
111A100W4	Steel fusion-welded tank without dome. Insulated. Gauging device. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 690 kPa (100 psi)
111A100F2	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Test pressure 690 kPa (100 psi)

* Canadian Transport Commission and Department of Transportation (U.S.)

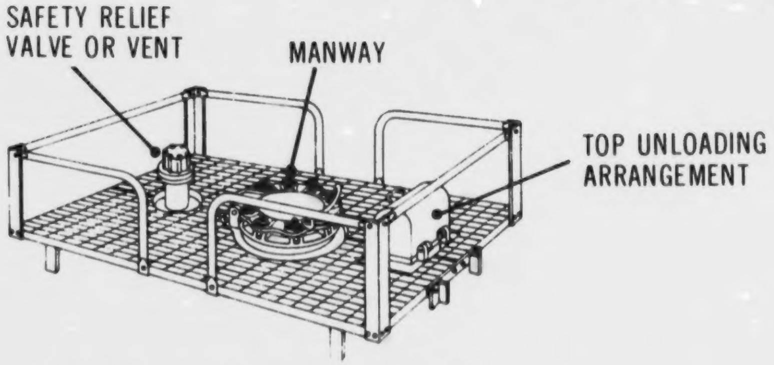
The railway tank cars usually used to transport 50 and 73 percent sodium hydroxide solutions have capacities ranging from 37 854 L (8000 gal.) to 90 900 L (20 000 gal.). Figure 8 shows a CTC/DOT 111A60W1 railway car used to transport sodium hydroxide solution; Table 3 indicates railway tank car details associated with this drawing (TCM 1979). Cars are equipped for unloading by pump or gravity flow through a 152 mm (6 in.) diameter bottom outlet provided with inner plug valves. This bottom discharge outlet may be furnished with steam jackets. In addition to bottom unloading, the cars may be unloaded from the top by compressed air. In this case, the sodium hydroxide is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve, usually a 51 mm (2 in.) threaded plug cock valve. Air pressure of 138 kPa (20 psi) is applied through the 25 mm (1 in.) air connection valve.

RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)


25 mm (1 in) AIR CONNECTION
51 mm (2 in) OUTLET
VACUUM RELIEF VALVE

Detail of top unloading arrangement


SAFETY RELIEF VALVE OR VENT
MANWAY
TOP UNLOADING ARRANGEMENT

Detail of loading platform

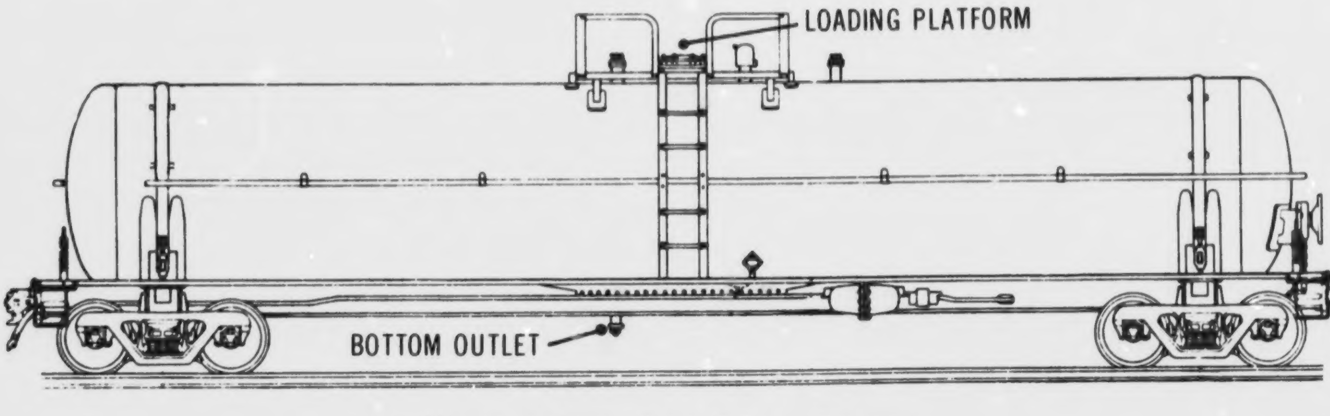

LOADING PLATFORM
BOTTOM OUTLET

Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. gal.)					
Description	16 700		17 200		20 000	
Overall						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L	(20 000 gal.)
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg	(85 800 lb.)
Car weight - (max.)	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	Steel		Steel		Steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
Approximate Dimensions						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centers	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)	2-3 m	(8-10 ft.)
Width of grating	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)	1.5-2 m	(5-6 ft.)
Loading/Unloading Fixtures						
Top Unloading						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)	203-356 mm	(8-14 in.)
Air connection	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)	25-51 mm	(1-2 in.)
Bottom Unloading						
Bottom outlet	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)	102-152 mm	(4-6 in.)
Safety Devices	Safety vent or valve		Safety vent or valve		Safety vent or valve	
Dome	None		None		None	
Insulation	Optional		Optional		Optional	

Railway tank cars transporting 73 percent sodium hydroxide solution are very similar to those in 50 percent caustic service, with the exception of the construction materials used.

Materials of construction for the tank are dependent upon the grade of solution. For 50 percent sodium hydroxide solution, a flange quality steel is required, usually ASTM A-283 Grade C steel plate with a 3 mm (0.1 in.) corrosion allowance (SCS 1963). For 73 percent sodium hydroxide solution, 316 stainless steel or Monel alloys are most suitable. Tanks may be constructed of steel with an inner nickel liner; steel tanks may be lined with caustic-resistant material.

Outside heating coils and glass wool insulation may be used for 50 percent and are required for the 73 percent sodium hydroxide solutions. Constructed from 203 mm (8 in.) diameter type A53 grade B steel pipe in half-oval form, the heating coils are laid out in a serpentine configuration across the bottom third of the tank (TCM 1979).

A safety relief valve set at 241 kPa (35 psi) or a safety vent set at 414 kPa (60 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, is also required. The top unloading arrangement must be protected by a housing covering the air connection valve and the unloading connection valve (TCM 1979). The maximum pressure allowable for the CTC/DOT 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60W1 or 111A60F1 cars are used, this maximum pressure would be 276 kPa (40 psi). Both these pressures exceed the maximum compressed air pressure of 138 kPa (20 psi) used during unloading. Sodium hydroxide solutions are never transported under pressure.

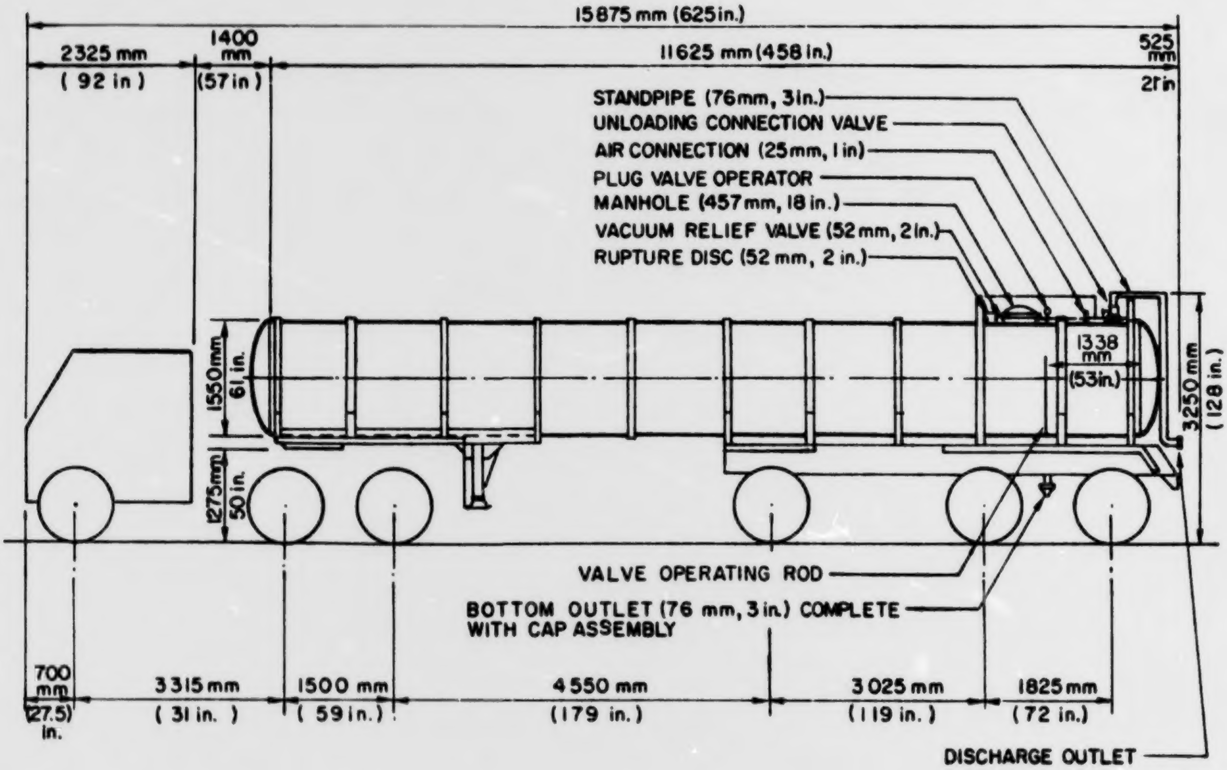
4.1.1.2 Tank motor vehicles. Although sodium hydroxide solutions are often shipped in railway tank cars, the 50 percent solution, and less frequently the 73 percent solution, are usually shipped by tank motor vehicle.

The capacity of tank trucks transporting sodium hydroxide solutions is dependent upon the specific gravity of the solution and the number of axles, usually two and sometimes three. Both these factors determine the gross vehicle weight, a summation of the sodium hydroxide solution weight, the tanker, the chassis and the tractor.

A tri-axle tank truck with a total gross weight of 50 000 kg (110 000 lb.) is shown in Figure 9. This 20 700 L (5 000 gal.) capacity tanker is the largest size allowable for a 73 percent sodium hydroxide carrier. A larger capacity tanker is conceivable for the 50 percent solution.

FIGURE 9

TANK MOTOR VEHICLE


15875 mm (625 in.)
2325 mm (92 in)
1400 mm (57 in)
11625 mm (458 in.)
525 mm 21 in
STANDPIPE (76 mm, 3 in.)
UNLOADING CONNECTION VALVE
AIR CONNECTION (25 mm, 1 in)
PLUG VALVE OPERATOR
MANHOLE (457 mm, 18 in.)
VACUUM RELIEF VALVE (52 mm, 2 in.)
RUPTURE DISC (52 mm, 2 in.)
1338 mm (53 in.)
1550 mm 61 in.
1275 mm 50 in.
3250 mm (128 in.)
VALVE OPERATING ROD
BOTTOM OUTLET (76 mm, 3 in.) COMPLETE WITH CAP ASSEMBLY
700 mm (27.5) in.
3315 mm (31 in.)
1500 mm (59 in.)
4550 mm (179 in.)
3025 mm (119 in.)
1825 mm (72 in.)
DISCHARGE OUTLET

ESTIMATED WEIGHT SUMMARY	
LOAD (20203L AT 1.76 kg/L)	35600 kg (78,400 lb)
TANK	3400 kg (7,500 lb)
CHASSIS	3800 kg (8,300 lb)
TRACTOR	7300 kg (16,000 lb)
TOTAL	50000 kg (110,000 lb)

TANK SPECIFICATIONS	
CAPACITY	22700L (5000 imp gal.) + 3%
COMPARTMENTS	ONE
BAFFLES	3mm - 5mm (1/8 - 3/16 in) DISHED
REINFORCING RINGS	S.S. - MC 312
HEADS	5mm (3/16 in) - SS 316
SHELL	10ga. - S S 316
CODE	MC 312, ASME
WORKING PRESSURE	207 kPa (30 psi)
WELD FINISH	W2 (VACUBLAST) INSIDE & OUTSIDE
TANK TO BE COVERED WITH FIBERGLASS INSULATION (76 mm, 3 in.) AND STAINLESS STEEL JACKET	

The double axle type vehicle is the most common carrier of caustic solutions. Tankers carrying 50 percent solution range in capacity from 9000 to 15 000 L (2000 to 3500 gal.) or from 13 600 to 24 200 kg (30 000 to 53 000 lb.) net mass, respectively.

Similar to railway tank cars, these trailers are unloaded through a bottom outlet provided with an inner plug valve. When compressed air is used for unloading, the 76 mm (3 in.) standpipe is used. The air connection is a 25 mm (1 in.) diameter screwed fitting located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied. Because tank trucks are used for hauling sodium hydroxide solutions relatively short distances, no steaming facilities are usually provided; however, insulation is required to keep heat losses to a minimum.

Tank motor vehicles must conform to DOT specifications TC312 or MC312 as outlined in Table 4 (TDGC 1980). The materials of construction and thickness of material are similar to those in use for railway tank cars. Sodium hydroxide solutions are not transported under pressure. Highway tankers must be pressure tested at 311 kPa (45 psi) minimum to allow for the compressed air pressure of 207 kPa (30 psi) used during top unloading. The maximum working pressure of the tanker is in effect 207 kPa (30 psi).

4.1.1.3 **Portable tanks.** Portable tanks are used to transport small volumes of sodium hydroxide solution. The capacities and weights of tanks vary depending on the user's requirements. Unloading fittings and methods are similar to those discussed for railway tank cars and highway tankers.

Portable tanks must conform to DOT specifications TC57 or TC60, or CTC specification 60. Table 5 lists descriptions under each specification (TDGC 1980).

Materials of construction are dependent upon the grade of solution. For 50 percent sodium hydroxide solution, a flange quality steel is normally used. For 73 percent sodium hydroxide solution, 316 stainless is required. The thickness of material for the cylindrical portion of the shells and tank ends must not be less than 9 mm (0.35 in.) for steel or the equivalent thickness for stainless or other material.

Metal portable tanks or closed bins may be used to carry anhydrous sodium hydroxide. Gross weight must not exceed 3175 kg (4000 lb.). Rubber-lined metal tanks or fibreglass tanks may also be used, providing capacities do not exceed 2.1 m^3 (75 cu. ft.)

4.1.2 **Packaging** (CTC 1974, for rail; TDGC 1980, for other modes; Kirk-Othmer 1978). In addition to bulk shipments, solution and anhydrous sodium hydroxide are also transported in other specialized containers as described in Tables 6, 7, 8 and 9. In the solid form, the material can be shipped as a single dense unit conforming to the size and

TABLE 4 TANK MOTOR VEHICLE SPECIFICATIONS

Transport Canada Specification Number	Description
TC312 (MC312)	Steel or stainless steel butt-welded tanks. Design and construct in accordance with ASME Code. Unloading should be done at pressures under 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment as required by ASME Code. One miminum 380 mm (15 in.) diameter manhole per compartment.

TABLE 5 PORTABLE TANK SPECIFICATIONS

Transport Canada Specification Number	Description
TC57	Steel, butt-welded, fusion-welded. Minimum tank capacity 400 L (88 gal.). Maximum tank capacity 2 400 L (528 gal.). Minimum one pressure relief device. Discharge valves require cap or plug.
TC60	Steel fusion-welded or seamless. Design and construct in accordance with ASME Code. Tank and permanent attachments to be postweld. Heat treated as a unit. 1% dome. Bottom discharge outlets prohibited except for acid corrosive liquids. Bottom washout optional. Minimum one pressure relief device. Test pressure 414 kPa (60 psi).

shape of the container and as flakes, beads or pellets. The latter forms can be shipped in various containers as well as in bulk hopper-type or pneumatic vehicles. The single dense unit is produced by pouring molten sodium hydroxide into a drum and allowing it to solidify. Upon receipt, the drum is stripped away to yield a solid block of sodium hydroxide (Kirk-Othmer 1978).

A table of steel drum sizes is indicated in Table 8. Fibre drum sizes are indicated in Table 9 (TDGC 1980). A typical steel drum is depicted in Figure 10.

TABLE 6 CONTAINER SPECIFICATIONS FOR ANHYDROUS SODIUM HYDROXIDE (CTC 1974 - 73.245b Corrosive Solids not Specifically Provided For)

Type of Container	Description
Metal, wooden or fibreboard	Box or case with inside containers which must be earthenware, glass, metal, plastic or fibre- or composition board; not more than 4.54 kg (10 lb.) net weight capacity each
Fibreboard	Box with one side paper bag, not more than 22.7 kg (50 lb.) net weight capacity
Fibreboard	Box with one side plastic bag, not more than 54.4 kg (120 lb.) net weight capacity
Metal	Drum, not over 0.205 m^3 (7 cu. ft.) capacity
Fibre	Drum, not exceeding 249.5 kg (550 lb.) net weight and not over 0.25 m^3 (8.8 cu. ft.) capacity
Plastic	Drum or pail, not exceeding 36.3 kg (80 lb.) net weight and not over 0.0273 m^3 (1 cu. ft.) capacity
Paper	Multiwall bag, not exceeding 49.9 kg (110 lb.) net weight, of at least 4-ply construction including moisture-barrier ply. Completed package filled to weight with product and closed for shipment must be able to withstand four drops from a height of 1.22 m (4 ft.) onto a solid surface, one drop on each end and one drop on each face, without sifting or rupture
Burlap	Bag, with inside plastic liner, made of not less than 0.213 kg (0.5 lb.) burlap, not exceeding 49.9 kg (110 lb.) net weight capacity. Same drop test specification as above
Plastic	Bag, not exceeding 49.9 kg (110 lb.) net weight capacity. Same drop test specification as above
Metal	Tank, portable, not over 3.0 m^3 (100 cu. ft.) capacity and 3 175 kg (7 000 lb.) gross weight. See section 4.1.1.3

Note: Hopper-type or pneumatic bulk vehicle, or metal, sift-proof tank cars, hopper type cars or pneumatic bulk cars approved by the Committee. See section 4.1.1.1.

TABLE 7 CONTAINER SPECIFICATIONS FOR SODIUM HYDROXIDE SOLUTIONS (CTC 1974 - 73.249 Alkaline Corrosive Liquids, n.o.s., Alkaline Caustic Liquids, n.o.s., Alkaline Corrosive Battery Fluids and Sodium Aluminate, Liquid)

Type of Container	Designation	Description
Glass	1A, 1B, 1C or 1E	Carboys in boxes, kegs or plywood drums
	IX	Boxed carboys; single trip for expert only
Glass	1D	Boxed carboys; not over 2.5×10^{-2} m^3 (0.9 cu. ft.) nominal capacity which must be closed
Metal	1H	Crate with inside polyethylene container spec. 2T.
Metal	5, 5A, 5C or 5M	Barrels or drums, with openings not exceeding 5.84×10^{-2} m (2.3 in.) in diameter
Metal	5D	Barrels or drums, rubber-lined
Metal	5H	Barrels or drums, lead-lined
Steel	6D or 37 M	Cylindrical overpacks, nonreusable, with inside polyethylene container spec. 2S or 2SL
Wood	10A	Barrels or kegs, lined with asphalt, paraffin or wax impervious to the lading
Wood	11A or 11B	Barrels or kegs, inside containers of glass or earthenware, not over 9.09×10^{-3} m (0.3 cu. ft.).
Fibreboard	12A	Boxes with inside glass, polyethylene, or other nonfragile plastic bottles not over 4.546×10^{-3} m^3 (0.15 cu. ft.) each Not more than 4 inside glass bottles exceeding 2.37×10^{-3} m^3 (0.08 cu. ft.) capacity each shall be packed in the outside container
Fibreboard	12B	Boxes with inside glass containers of not over 4.546×10^{-4} m^3 (0.015 cu. ft.) capacity each Boxes, with not more than one glass inside container not over 4.546×10^{-3} m^3 (0.15 cu. ft.) capacity containing NaOH solution not over 25 percent strength Boxes with inside containers of polyethylene or other nonfragile plastic material resistant to the lading, and having threaded closures or

TABLE 7 CONTAINER SPECIFICATIONS FOR SODIUM HYDROXIDE SOLUTIONS (Cont'd)

Type of Container	Designation	Description
		other equally efficient type closure, not over 4.546 x 10^{-3} m^3 (0.15 cu. ft.) capacity each. Gross weight of complete package must not exceed 29.48 kg (65 lb.) Boxes with inside polyethylene containers spec. 2U not over 2.273 x 10^{-2} m^3 (0.8 cu. ft.) capacity each Boxes with inside polyethylene bottles, not over 2.273 x 10^{-2} m^3 (0.8 cu. ft.) capacity each, as specified by paragraph 34 of spec. 12B. Not more than bottle per outside box
Wood	15A, 15B, 15C, 16A or 19A	Boxes with glass or earthenware inside containers, not over 9.092 x 10^{-3} m^3 (0.3 cu. ft.) each, or with metal inside containers not over 2.273 x 10^{-2} m^3 (0.8 cu. ft.) each Boxes with inside containers of polyethylene of capacity not over 4.546 x 10^{-3} m^3 (0.15 cu. ft.) each Boxes with inside containers of glass, earthenware, polyethylene or other nonfragile plastic material (bags are not authorized) not over 4.546 x 10^{-3} m^3 (0.15 cu. ft.) each, except that inside containers up to 1.364 x 10^{-2} m^3 (0.5 cu. ft.) are authorized when only one is packed in each outside container
Wood	15P or 22C	Box, wood or glued plywood or plywood drum with polyethylene container
Wood	16A	Box, wirebound with inside polyethylene container spec. 2U
Wood	16D	Wirebound overwrap with inside polyethylene container
Metal	17C, 17E or 17F	Drum, single trip, with openings not exceeding 5.8 x 10^{-2} m (2.3 in.) in diameter
Metal	17H, 37A or 37B	Drums, single-trip, welded side seams, not over 2.273 x 10^{-2} m^3 (0.8 cu. ft.) capacity each

TABLE 7 CONTAINER SPECIFICATIONS FOR SODIUM HYDROXIDE SOLUTIONS (Cont'd)

Type of Container	Designation	Description
		Must be lined with a pliable plastic impervious to lading
Fibre	21P	Drum overpack with inside polyethylene container spec. 2S, 2SL or 2U
Glass	33A	Polystyrene case, nonreusable container, having one inside container, not over 4.732 x 10^{-4} m^3 (0.015 cu. ft.) capacity
Polyethylene	34	Container, without overpack, not over 1.137 x 10^{-1} m^3 (4 cu. ft.) capacity
Steel	37P	Drums with polyethylene liner, nonreusable
Rubber	43A	Drums

TABLE 8 STEEL DRUM SIZES

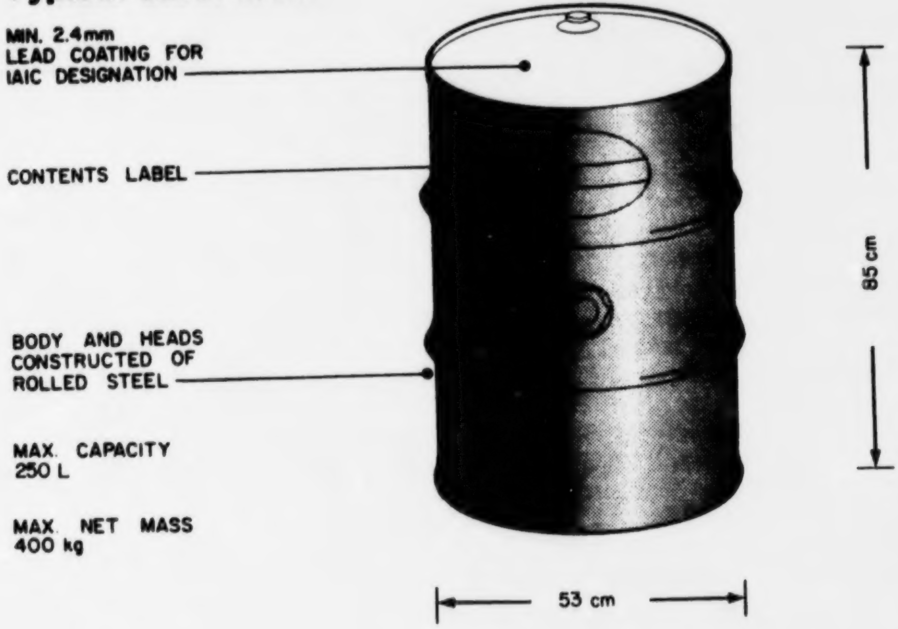
Form of Anhydrous Sodium Hydroxide	Weight in kg (lb.)			Drum in Size in mm (in.) Diameter x Height	Gauge of Steel
	Net	Tare	Gross		
Solid	318 (700)	10 (22)	328 (722)	525 x 788 (20 x 30)	24
Flake	45 (100)	4 (9)	49 (109)	369 x 588 (15 x 23)	24
	182 (400)	10 (22)	192 (422)	525 x 838 (20 x 33)	24
Crystal	182 (400)	10 (22)	192 (422)	525 x 838 (20 x 33)	24

TABLE 9 FIBRE DRUM SIZES

Form of Anhydrous Sodium Hydroxide	Net Weight in kg (lb.)	Drum Size in mm (in.) Diameter x Height
Flake	45 (100)	369 x 588 (15 x 23)
	182 (400)	525 x 838 (20 x 33)
Crystal	182 (400)	525 x 838 (20 x 33)

FIGURE 10

TYPICAL DRUM CONTAINER



Typical steel drum

MIN. 2.4mm
LEAD COATING FOR
IAIC DESIGNATION
CONTENTS LABEL
BODY AND HEADS
CONSTRUCTED OF
ROLLED STEEL
MAX. CAPACITY
250 L
MAX. NET MASS
400 kg
85 cm
53 cm

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (Dow 1980; Hooker PIM):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, adequate lighting must be provided and an explosion-proof rating is recommended.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked and a derail employed.
- A safe operating platform must be provided at the unloading point.
- All personnel should be properly trained in the required safe-handling procedures for sodium hydroxide.
- All personnel should wear protective clothing and equipment.
- The unloading track should be level and the area surrounding the operation well-marked with caution signs.
- Eye wash fountain and safety shower should be available and tested.

Two means of off-loading are used for sodium hydroxide rail cars, top off-loading and bottom off-loading. Both means are indicated in Figure 11.

Most sodium hydroxide tank cars are equipped with an eduction pipe and can be unloaded through the dome by air pressure, or they can be unloaded through the bottom discharge outlet. Unloading through the bottom outlet valve can be accomplished by gravity flow to a pump or directly to the storage tank, with or without the aid of air pressure. The latter, of course, is possible only if the top of the storage tank is lower than the bottom of the tank car. Unloading through the dome by air pressure is satisfactory for the 50 percent solution, provided the total lift from the bottom of the tank car to the top of the storage tank is not more than 9 m (30 ft.). The 73 percent solution should be pumped (Dow 1980).

Proceed with top off-loading as follows:

- Remove the protective housing covering the air inlet and discharge line valves at the top of the car. Very carefully open the 25 mm (1 in.) air inlet connection to relieve and equalize the pressure. The temperature of the solution should be taken through the dome of the car in order to determine if heating is necessary. Heating should not be necessary if the temperature is above 29°C for the 50 percent solution and above 85°C for the 73 percent solution. Connect the 51 mm (2 in.) unloading line to the unloading line valve connection and the air line to inlet valve. Air pressure must be reduced to 138 kPa (20 psi) for unloading and a safety relief valve should be installed in the air line to release at 172.4 kPa (25 psi) (Hooker PIM; Dow 1980).
- After opening the unloading line valve, the air pressure can be slowly applied until there is a suitable flow of solution to the storage tank. Eliminate all air or solution leaks by tightening necessary fittings. Continue until the tank car is empty (Hooker PIM; Dow 1980).
- When the unloading line is completely drained, turn off the air supply and allow the system to come to atmospheric pressure, 101 kPa. Ensure the discharge line is completely drained (Hooker PIM; Dow 1980).
- Reverse the procedure to seal the tank car.

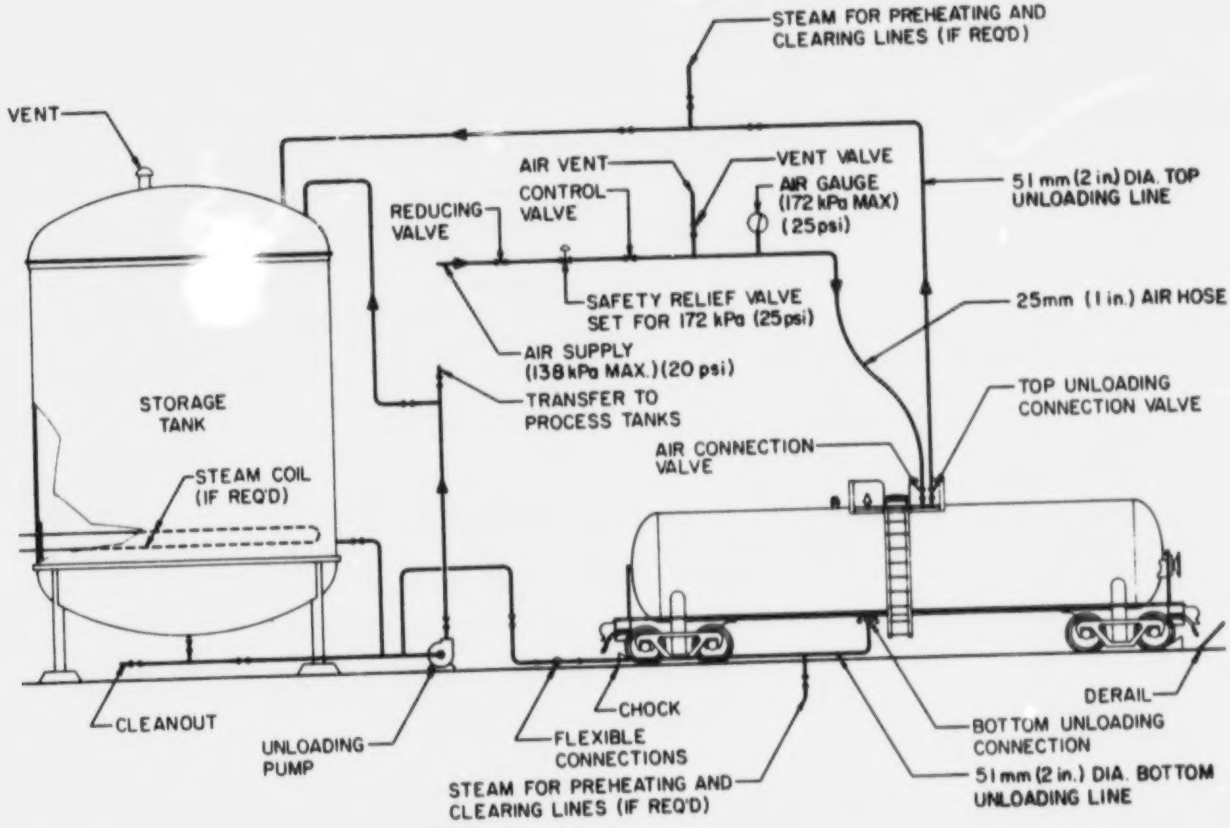
Proceed with bottom off-loading in the following manner using gravity flow or pumping (Hooker PIM; Dow 1980):

- Open the dome cover and ensure that it remains that way during the unloading operation.
- Heat the bottom discharge outlet thoroughly by connecting a steam line to the steam, jacket on the bottom discharge fitting. Steaming may not be necessary when unloading 50 percent solution.
- Check the plug cock on the bottom discharge outlet to ensure it is closed, and remove the plug or cap below the valve.

FIGURE 11

TANK CAR UNLOADING

Reference: HOOKER PIM


STEAM FOR PREHEATING AND CLEARING LINES (IF REQ'D)
VENT
AIR VENT
VENT VALVE
CONTROL VALVE
AIR GAUGE (172 kPa MAX) (25psi)
51 mm (2 in) DIA. TOP UNLOADING LINE
REDUCING VALVE
SAFETY RELIEF VALVE SET FOR 172 kPa (25psi)
25mm (1 in.) AIR HOSE
AIR SUPPLY (138 kPa MAX.)(20 psi)
TRANSFER TO PROCESS TANKS
STORAGE TANK
TOP UNLOADING CONNECTION VALVE
AIR CONNECTION VALVE
STEAM COIL (IF REQ'D)
DERAIL
CLEANOUT
CHOCK
BOTTOM UNLOADING CONNECTION
UNLOADING PUMP
FLEXIBLE CONNECTIONS
51 mm (2 in.) DIA. BOTTOM UNLOADING LINE
STEAM FOR PREHEATING AND CLEARING LINES (IF REQ'D)

NOTE:

1 - FOR TOP OR BOTTOM UNLOADING METHOD SEE TEXT.

- Attach the unloading line and preheat with steam.
- Open the inside bottom valve by turning the valve rod handle at the dome of the car. Open the plug cock on the bottom discharge outlet and allow the contents to flow to the pump or to the desired location. For the 73 percent solution, the dilution operation sometimes is started prior to this step, then the inside bottom valve is opened and the pump started.
- The pump is started and the unloading operation completed.
- Reverse the above procedure to seal the car. Remove all transfer line attachments.

Proceed with bottom off-loading through the bottom outlet by air pressure in the following manner (Hooker PIM; Dow 1980):

- The following is similar to the procedure for bottom off-loading by gravity or pump
    - heat the bottom discharge outlet;
    - open the dome cover;
    - cautiously remove the bottom plug;
    - attach the unloading line;
    - open the auxiliary valve.

Then proceed as follows:

- Replace and securely fasten the dome cover.
- Connect the air supply line to the air inlet on the manway.
- Open the bottom outlet valve operated from the top of the car.
- Apply air pressure until the car is empty.
- Shut off the air and allow the discharge to drain until the car reaches atmospheric pressure.
- Reverse the procedure to seal the car.

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles (Dow 1980). The unloading of sodium hydroxide tank trailers is similar to that of tank cars, with the exception that no facilities for steaming are usually provided. The general procedures for tank cars apply equally well to tank trailers.

The driver of the tank truck is usually responsible for his own unloading, requiring only a 51 mm (2 in.) male connector on the receiver's permanent unloading system. The same safety precautions required for railway tank car unloading should be adhered to.

4.2.3 Specifications and Materials for Handling and Storage Equipment. The materials of construction for handling system components and storage equipment discussed in this section along with specifications refer to those generally used in sodium hydroxide service. It is recognized that other materials may be used for particular applications. Most materials generally used are indicated in Table 10. The components of typical handling and storage equipment that are discussed in this subsection include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

The preferred metal for handling sodium hydroxide at all concentrations and temperatures, including molten anhydrous up to 480°C, is nickel. Its use, however, is limited due to high cost and availability problems. Generally, nickel or its alloys are used only for equipment that requires precision tolerances, for solutions at elevated temperatures, or where high solution velocities are encountered. The use of mild steel is usually adequate for most sodium hydroxide handling applications. The rate of corrosion of sodium hydroxide solutions on steel at ambient temperature is less than that of water (Kirk-Othmer 1978). Steel equipment is satisfactory for handling 50 percent solution at moderate temperature (<49°C) (Hooker PIM).

The use of steel is not recommended at temperatures above 49-60°C because of corrosion. The chrome-nickel stainless steels are more resistant to corrosion by sodium hydroxide than is mild steel. Monel 1 is very resistant to corrosion but tends to discolour 50 percent solution over an extended period due to the presence of copper in the metal. The following table shows the corrosion rates for various metals in contact with 50 percent sodium hydroxide solution. Tests were of 30 days duration at temperatures ranging from 55 to 75°C.

Material	Corrosion Rate, mg/dm^2/day
Inconel	0.10
Nickel	0.13
Monel	0.16
Cu-Ni (70-30)	0.31
Cr-Ni Steel (18-8)	0.57
Ni-resist (Type 1)	10.5
Mild Steel	43.4
Cast Iron	50.5

In general, corrosion resistance is proportional to nickel content. Aluminum, brass, bronze, copper, tin or zinc should not be used in contact with sodium hydroxide or its solutions. Hydrogen gas may be generated which can build up pressure and also form an explosive mixture with air (Kirk-Othmer 1978; Hooker PIM).

In addition to ordinary corrosion, the chloride present in regular diaphragm cell sodium hydroxide solutions may cause chloride stress corrosion cracking (also referred to as caustic embrittlement) of austenitic stainless steels at elevated temperatures. This occurs especially at points of unrelieved stress. Temperatures at which equipment (as-welded carbon steel) can be considered safe from failure due to stress corrosion cracking are shown in the following table:

Temperature °C	Solution Concentration (%)
93	7
88	10
71	20
60	30
52	40
49	50

Even at temperatures and concentrations at which no appreciable corrosion occurs, sodium hydroxide solutions will dissolve a small amount of iron from steel handling and storage equipment. This can be minimized by 1) reducing the contact time, 2) keeping the metal-solution interface to a minimum, 3) lowering the temperature, and 4) using liners. Typical materials used as liners are polypropylene, suitable to 79°C, and fluorocarbon plastics at moderately high temperatures (Kirk-Othmer 1978; Hooker PIM; Dow 1980).

The concensus among the references reviewed for 50 percent solution is that Schedule 40 carbon steel is recommended for pipes and fittings in sodium hydroxide service (Dow 1980; Hooker PIM; CCPA 1983). It was put forth, however, that some users/suppliers are using Schedule 80 (CCPA 1983). Cast iron pipe is not recommended for handling sodium hydroxide due to its brittleness (CCPA 1983). If iron contamination is a problem, flanged steel pipes with a polypropylene liner are recommended and suitable to

79°C. Unsupported plastic pipes should be used; fibreglass-reinforced plastic pipes should be used cautiously only for specific use conditions (Dow 1980). Flanged or welded joints (screwed connections have been used successfully) may be used for sodium hydroxide lines (CCPA 1983; Dow 1980). One supplier recommends the use of carbon steel, ASTM A 53, Type E or S, Grade B, Schedule 20 (203 mm through 305 mm (8 to 12 in.) pipe), Schedule 40 (through 15.24 cm (6 in.) pipe) and screwed construction (through 20 mm (3/4 in.) pipe) for 50 percent solutions. Thread dope recommended is TFE paste-type or TFE tape (Hooker PIM). Nickel or nickel-clad steel is recommended for use with 73 percent solution (Hooker PIM). Stress relief is recommended to increase the service life of piping systems. If a leak develops at a weld, the only satisfactory way to repair it is to chip out the bad weld and reweld or replace the section of pipe (SCS 1963).

All process piping should be installed above ground, where possible. When buried, cathodic protection will minimize exterior corrosion. Piping should be designed oversize to eliminate turbulent flow which may erode the hydroxide passivating (resistant to corrosion) surface that gradually forms on piping, thereby minimizing the chance for iron contamination. Large radius ells are also recommended to maintain laminar flow. Unloading lines should be 51 mm (2 in.) pipe, since this is the same size as the standard fitting on sodium hydroxide tank cars. Process piping may be other sizes; however, pipe under 25 mm (1 in.) is generally not recommended. Outdoor lines should be self-draining, heated and insulated. If self-draining is not feasible, capped drain valves should be installed at the lowest point in the system (Dow 1980; Hooker PIM; SCS 1963). Heating of outdoor lines can be accomplished by steam-tracing (Hooker PIM; CCPA 1983) or by self-regulating heating tape or heating tapes or cables with thermostatic control (Dow 1980). One reference states that steam-tracing is not normally recommended since the temperature of the sodium hydroxide can readily exceed 60°C under static condition, with eventual stress cracking in welded areas (Dow 1980). The steam line should be separated from the line transporting the sodium hydroxide by small pieces of insulation, e.g., magnesia block, spaced about 3 m (10 ft.) apart. Overheating of the transfer line can occur if the pipe and steam tracer come into contact, or are too close to one another. Insulation should be applied over the steam-traced line (Hooker PIM; CCPA 1983). Steam-trace lines may be copper tubing or steel pipes usually of 9 or 13 mm diameter (3/8 to 1/2 in.) (SCS 1963).

Flexible steel hose or solid pipes with swivel joints may be used for the flexible sections of the unloading line. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Some installations of flexible line are made with standard fittings using a number of threaded elbows. This will give sufficient flexibility but usually costs more to maintain because the threaded fittings leak easily (SCS 1963).

For valving of 50 percent sodium hydroxide solution lines, lubricated iron plug cocks or all iron gate valves will serve adequately. For hot solutions of 50 percent and all solutions of 73 percent sodium hydroxide, lubricated nickel plug cocks will give best service (SCS 1963).

Graphitized asbestos, as well as Teflon and rubber, can be used as gasket materials (CCPA 1983).

While steel or cast iron non-airbinding centrifugal pumps should be used for sodium hydroxide solutions, such pumps suffer from high maintenance costs and short service life. Optimum service is usually obtained from Alloy 20 or its equivalent. The pump should have an open impeller, a Monel shaft and an extra-deep stuffing box. It should also be provided with connections for steaming and draining. Close coupled pumps should not be used. If a pump is equipped with a packing gland, graphitized asbestos packing should be used. If "weeping" of sodium hydroxide from the packing gland will create a personnel safety hazard, pumps equipped with a mechanical seal should be used (Hooker PIM; Dow 1980). Positive displacement or other types of pumps may be used for specific conditions (Dow 1980).

Storage tanks should generally be of sufficient size to hold the contents of one tank car. Mild steel, butt-welded tanks are suitable for normal storage conditions. Annealing to prevent stress corrosion cracking is generally not required unless temperatures greater than 60°C will be encountered. Since 73 percent sodium hydroxide solution freezes above this temperature, serious corrosion of ordinary steel will occur and the use of nickel or nickel-clad steel or a resistant lining is recommended. Cylindrical tanks, either horizontal or vertical, are satisfactory although the latter are usually preferred since they take up less space and are easily supported on concrete slabs. Tank bottoms should be set in an asphalt grout to protect against exterior corrosion. Storage tanks should be fitted with heating equipment and insulated (Dow 1980; Hooker PIM).

4.3 Compatibility with Materials of Construction

The compatibility of sodium hydroxide with materials of construction is shown in Table 10. Unbracketed abbreviations are derived from Table 11. The rating system for the materials is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 10 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	50%	≤49	CS ASTM A53		
	50%	<66	CS ASTM A106 (DCS)		
		79	Chlorinated Polyether*		
		79	PP (DOW 1980) PVDF* (DCRG 1972)		
		93	PVDF* (DCRG 1972) SS 304, 316 (CE 1980)		
	70%	To materials operating limit	PVC I PE* (MWPP 1978)		
	73%	49	PE* (DPPED 1967)		
		60	PVC* (DPPED 1967)		
		60	PVC II* (DPPED (1967)		
		66	PVDF, PP* (DCRG 1972)		
		71	ABS* (DPPED 1967)		
		79	Chlorinated Polyether* (DCRG 1972)		

TABLE 10 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)	All Anhydrous	<316°C	Ni 200 (CE 1980)		
		>316°C	Ni 201 (CE 1980)		
		≤480°C	Ni (Kirk-Othmer 1978)		CI (CCPA 1983)
2. Valves	50%	Moderate	All-iron (DCS)		
	50%	<49°C	CI, Steel (Hooker PIM)		
	50%	Hot, >49°C	Nickel (DCS; Hooker PIM)		
	73%		Nickel (Hooker PIM)		
3. Pumps	Aqueous		Body: All-Iron, SS 410, SS 304, SS 316, CI, Monel, Nickel (HIS 1969)		
			Wetted Parts: Monel, Nickel-CI (DCS)		
			Alloy 20 or equivalent (Dow 1980)	Steel, CI (Dow 1980)	
4. Storage	50%	<66	CS (DCS)		
		<60	Mild Steel (Dow 1980)		
		≤49	Steel ASTM A283 Grade C (Hooker PIM)		
		>49	Nickel (Hooker PIM)		
	73%	>62	Nickel (Hooker PIM)		

TABLE 10 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
4. Storage (Cont'd)	50-73%	not stated	Neoprene Latex (20 mil lining) (CE 1980) NR, CR (linings) (CE 1980) 10 mm Steel Plate of Flange Quality (SCS 1963)		
5. Others	5%	52, 100	Concrete (CDS 1967)		
		24	Wood (CDS 1967)		
	5	100	TA (FMT)		
	7%	<93	Steel (Hooker PIM)		
	10%	24 to 79	Wood (CDS 1967)		
		<88	Steel (Hooker PIM)		
	10% to 20%	52	Zr		Glass (CDS 1967)
	10% to 25%	boiling	Ti, Zr (FMT)		
	10% to 30%	24	Concrete (CDS 1967)		
	20	<71	Steel (Hooker PIM)		
	50%	79	Chlorinated Polyether, PP (DCRG 1972)		
		93	PVDF (DCRG 1972)		
		boiling	Allcorr, Hastelloy B-2,		SS 302 SS 304 (ASS)

TABLE 10 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	50%	boiling	Inconel 625 (TA)		
		100	CPVC (TPS 1978)		
	70%	22	CPVC (TPS 1978)		
		100			Glass (CDS 1967)
	73%	66	PVDF PP (DCRG 1972)		
		79	Chlorinated Polyether (DCRG (1972)		
	Viscous Solution	60	PE, PP POM, NBR* IIR, EPDM CR*, FPM CSM* (GF)	uPVC (GF)	NR (GF)
	All	20	SS 316 SS 302 SS 304 SS 410 SS 430 (ASS)		
	≤ pH 14	65.5	Glass on Steel (alkali resistant) (CE 1980)		
	≤ pH 13	82	Glass on Steel (alkali resistant) (CE 1980)		
	≤ pH 13	100		Glass on Steel (alkali resistant) (CE 1980)	
	≤ pH 11	82	Glass on Steel (older acid/alkali-resistant) (CE 1980)		

TABLE 10 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	100%	289			Glass (CDS 1967)
	100% (Assumed)	Melting, 315		SS 316 (ASS)	SS 302 SS 304 (ASS)
			IIR Si EPDM (GPP)		NR, SBR CR, NBR CSM (GPP) Zinc Brass Bronze (SCS 1963) Aluminum Tin (HCS 1980)

* This material has been given a lower rating in a similar application by another reference.

TABLE 11 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Aluminum
	Brass
	Bronze
CI	Cast Iron, Austenitic
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
	Copper-Nickel (70-30)

TABLE 11 MATERIALS OF CONSTRUCTION (Cont'd)

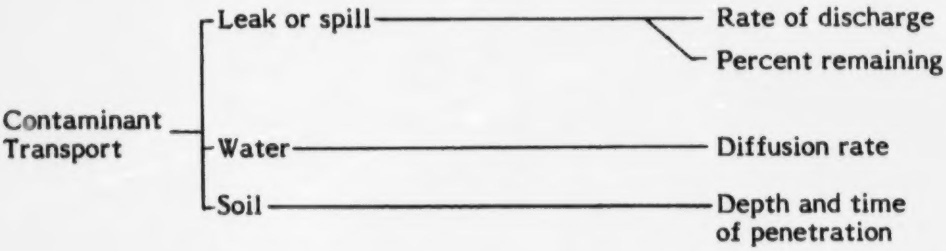
Abbreviation	Material of Construction
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
	Inconel
	Iron
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene Rubber (Nitrile, Buna N)
NR	Natural Rubber
	Neoprene Latex
	Nickel
	Nickel-Copper Alloy (Monel)
	Nickel-resist (Type 1)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
Si	Silicon
	Steel
	Steel, Cr-Ni (18-8)
SBR	Styrene/Butadiene (GR-5, Buna N)
SS (Followed by grade)	Stainless Steel
	Tin
uPVC	Unplasticized Polyvinyl Chloride
	Wood
	Zinc

5 CONTAMINANT TRANSPORT

5.1 General Summary

Sodium hydroxide is transported in solid, flake or bead form, and as 50 and 73 percent aqueous solutions; 73 percent sodium hydroxide is heated prior to shipment to keep it above its freezing point of 62°C, and may have to be heated prior to off-loading. When spilled in water, all forms will dissolve rapidly. When spilled on soil, the liquid forms will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Sodium hydroxide in the water table may be an environmental concern. Because sodium hydroxide is essentially nonvolatile under normal conditions, dispersion in air is not considered to be a problem.

Factors considered for the transport of a sodium hydroxide spill in water and on soil are:



5.2 Leak Nomograms

5.2.1 Introduction. As mentioned above, sodium hydroxide is transported as flakes or beads, or as an aqueous solution at 50 or 73 percent concentrations. In aqueous form, sodium hydroxide is commonly transported in cylindrical railway tank cars and tank motor vehicles. While the capacities of the tank cars vary widely, one tank car has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. This car has been used throughout the EnviroTIPS series to allow for comparisons between various chemicals.

If a tank car loaded with 50 percent aqueous solution is punctured on the bottom, all of the contents will drain out by gravity. Higher concentrations of sodium hydroxide solution are highly viscous or are solid at normal temperatures; they will not drain by gravity unless the temperature is elevated. Consequently, the leak nomograms apply only to the 50 percent solution (or any more dilute form) at temperatures above 11°C, or to the 73 percent solution at temperatures above 62°C.

The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the low volatility of sodium hydroxide solution and the fact that tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

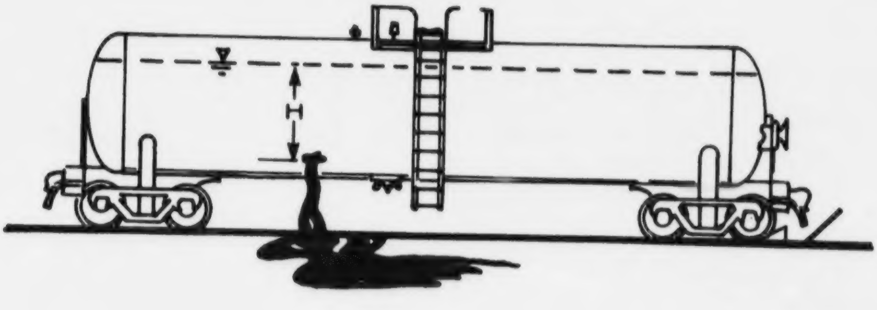


FIGURE 12 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). The venting rate (q) is a function of the hole size (A) and shape, the height of the fluid above the puncture hole (H), and a coefficient of discharge (Cd). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2 Nomograms.

5.2.2.1 Figure 13: Percent remaining versus time. Figure 13 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m Ø x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80 000 L of 50 percent sodium hydroxide solution. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 14: Discharge rate versus time. Figure 14 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations

i) Problem A

The standard tank car (2.75 m Ø x 13.4 m long) filled with a 50 percent aqueous solution of sodium hydroxide has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 13
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 14
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

Note: At lower temperatures, sodium hydroxide solutions are very viscous and would discharge at a slower rate. At still lower temperatures, the solutions will solidify, stopping the discharge.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, sodium hydroxide will dissolve rapidly. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to

FIGURE 13

SODIUM HYDROXIDE

PERCENT REMAINING VS TIME

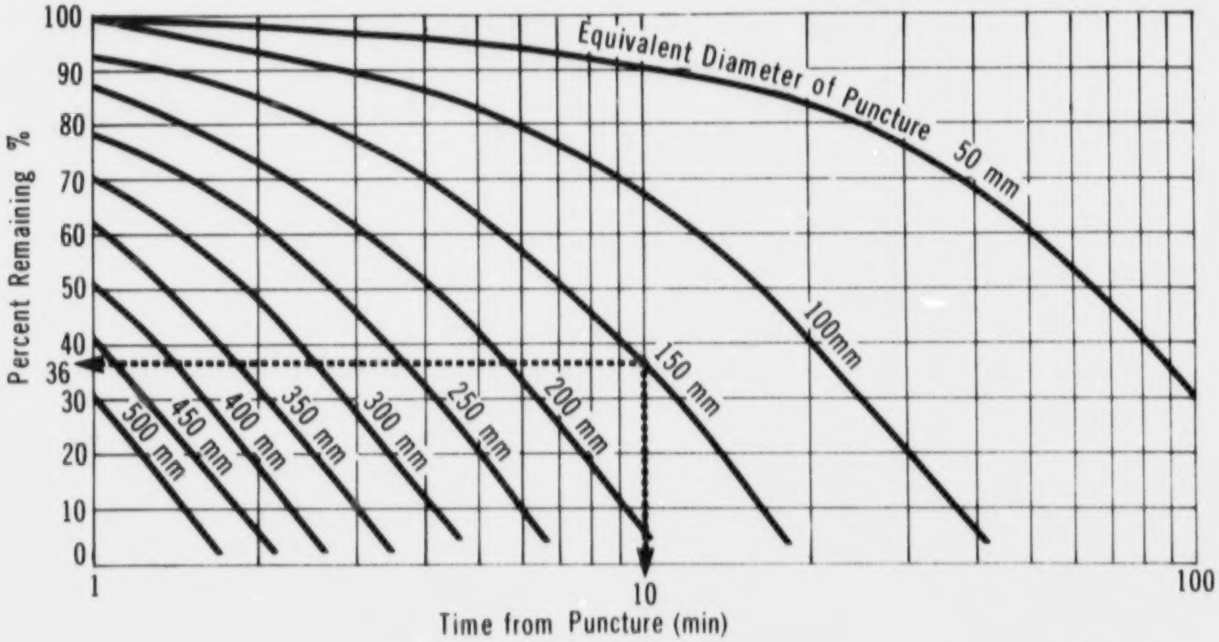
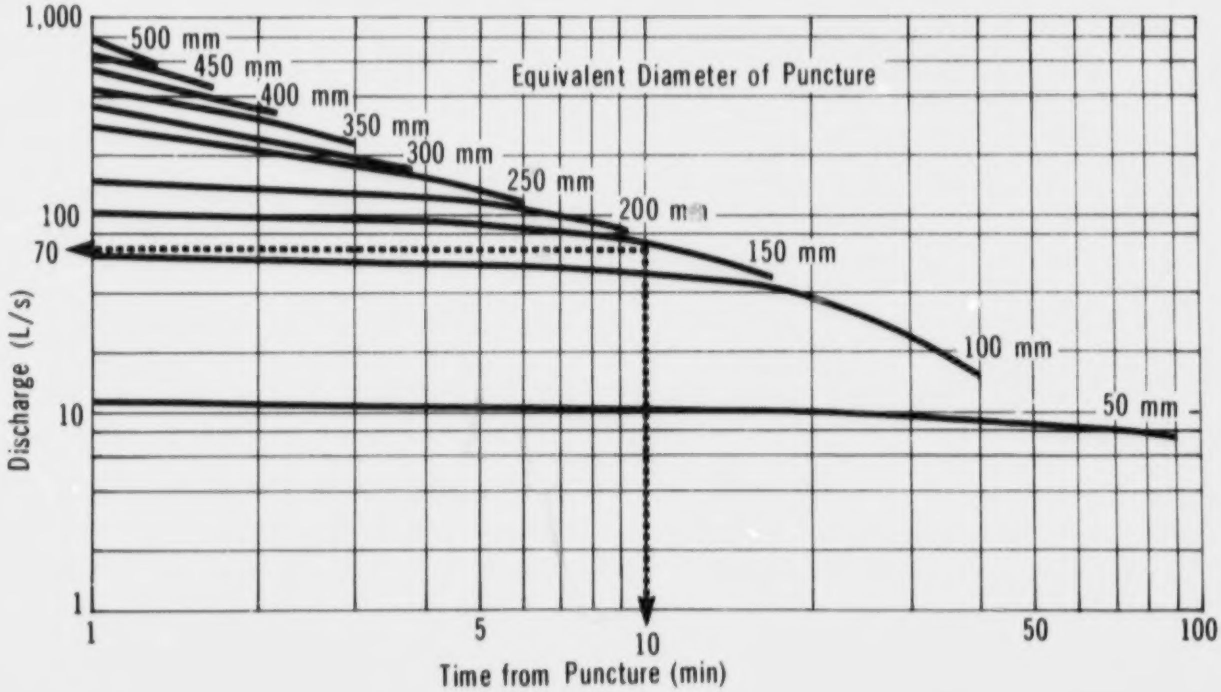


FIGURE 14

SODIUM HYDROXIDE

DISCHARGE RATE VS TIME



neutrally buoyant liquids and solids that dissolve in water. As sodium hydroxide is denser than water, the maximum concentration would be expected near the bottom.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-Tidal Rivers

Figure 16: time versus distance for a range of average stream velocities

Figure 17: hydraulic radius versus channel width for a range of stream depths

Figure 18: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 19: alpha versus diffusion coefficient for various time intervals

Figure 20: alpha versus delta for a range of spill sizes

Figure 21: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 22: volume versus radius for the hazard zone for a range of lake depths

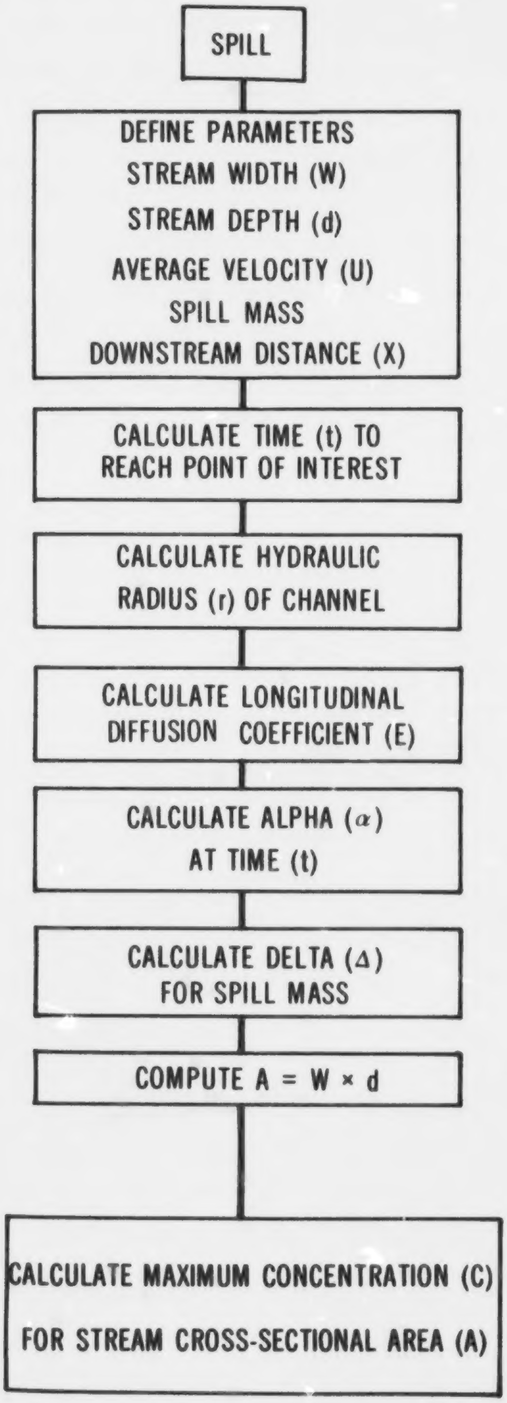
Figure 23: average concentrations versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 15 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 16 through 21) are described in the following sub-sections.

5.4.2.1 Nomograms for non-tidal river.

Figure 16: Time versus distance. Figure 16 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = __________ m

d = __________ m

U = __________ m/s

MASS = __________ tonnes

X = __________ m

Step 2: Use Figure 16

t = __________ minutes

Step 3: Use Figure 17

r = __________ m

Step 4: Use Figure 18

E = __________ m^2/s

Step 5: Use Figure 19

α = __________

Step 6: Use Figure 20

Δ = __________

Step 7: Compute stream cross-sectional Area (A)

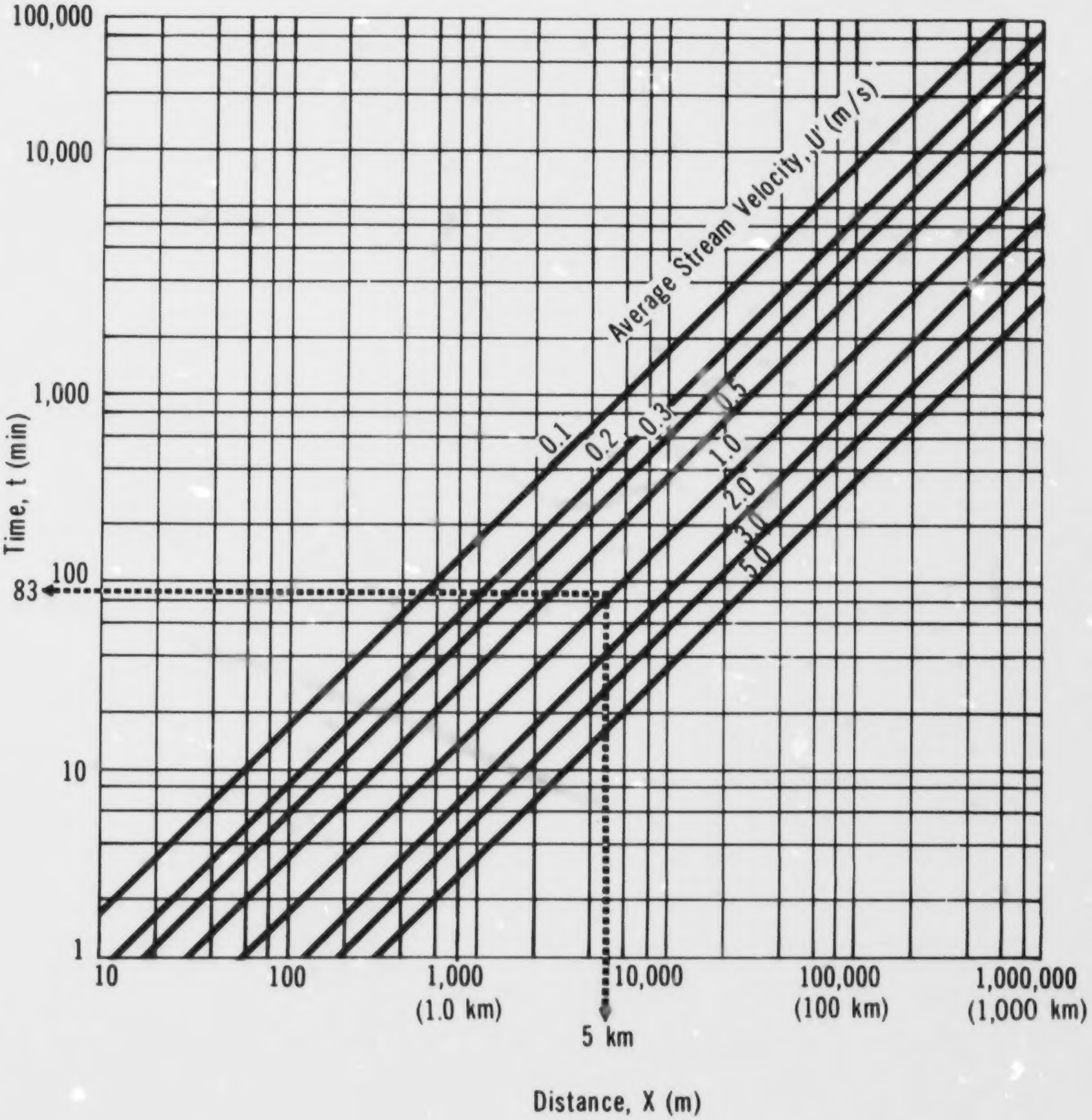
A = W × d _____ m^2

Step 8: Use Figure 21

C = __________ ppm

SODIUM HYDROXIDE

TIME vs DISTANCE



stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 16.

Figure 17: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 17 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 18: Diffusion coefficient versus hydraulic radius. Figure 18 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 17 and the average stream velocity (U).

Figure 19: Alpha versus diffusion coefficient. Figure 19 is used to estimate a conversion factor alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 20: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 20 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 21: Maximum concentration versus delta. Figure 21 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 21 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

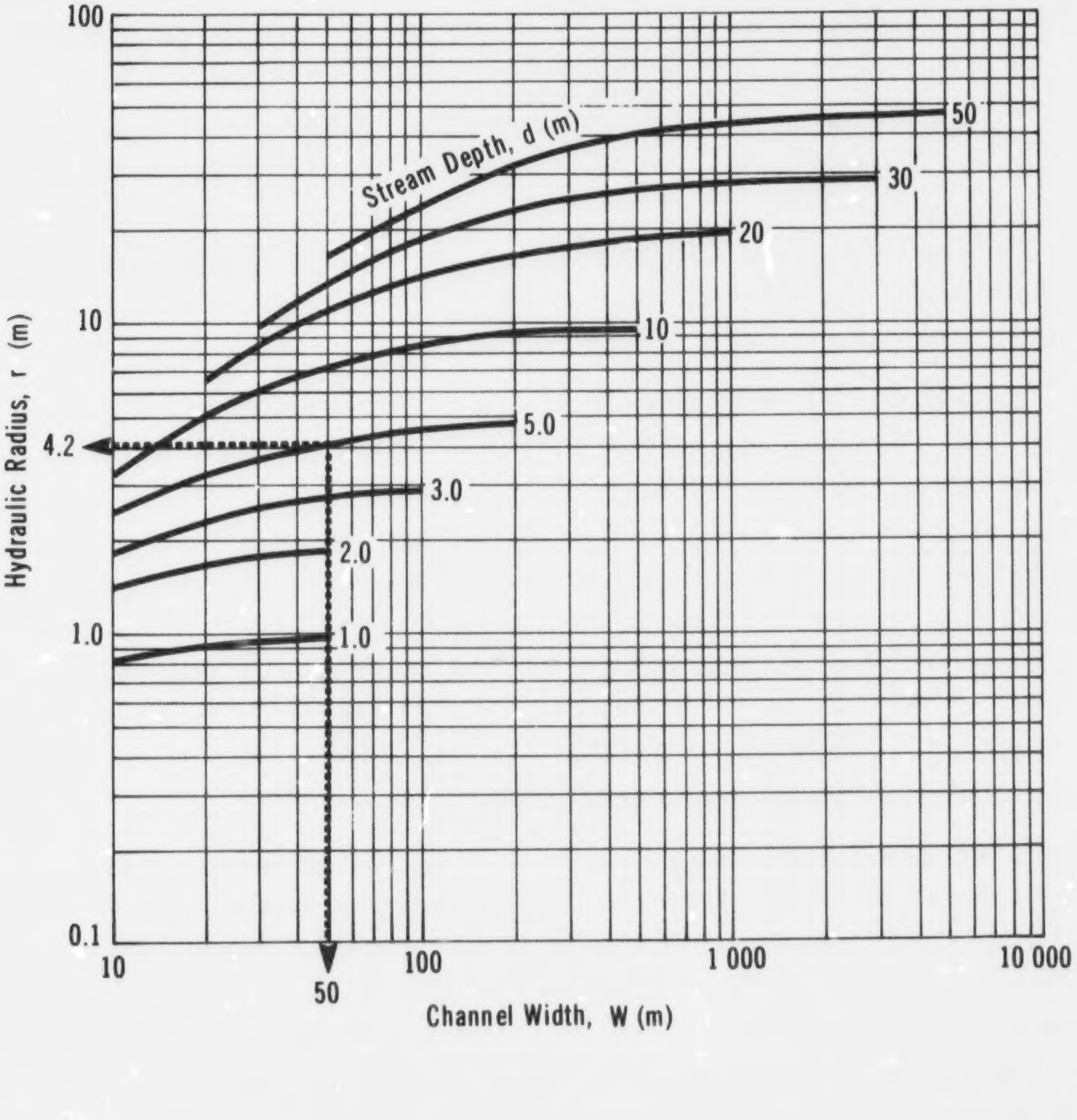
5.4.2.2 Nomograms for lakes or still water bodies.

Figure 22: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 22. The radius (r) represents the distance from the spill to the point of interest.

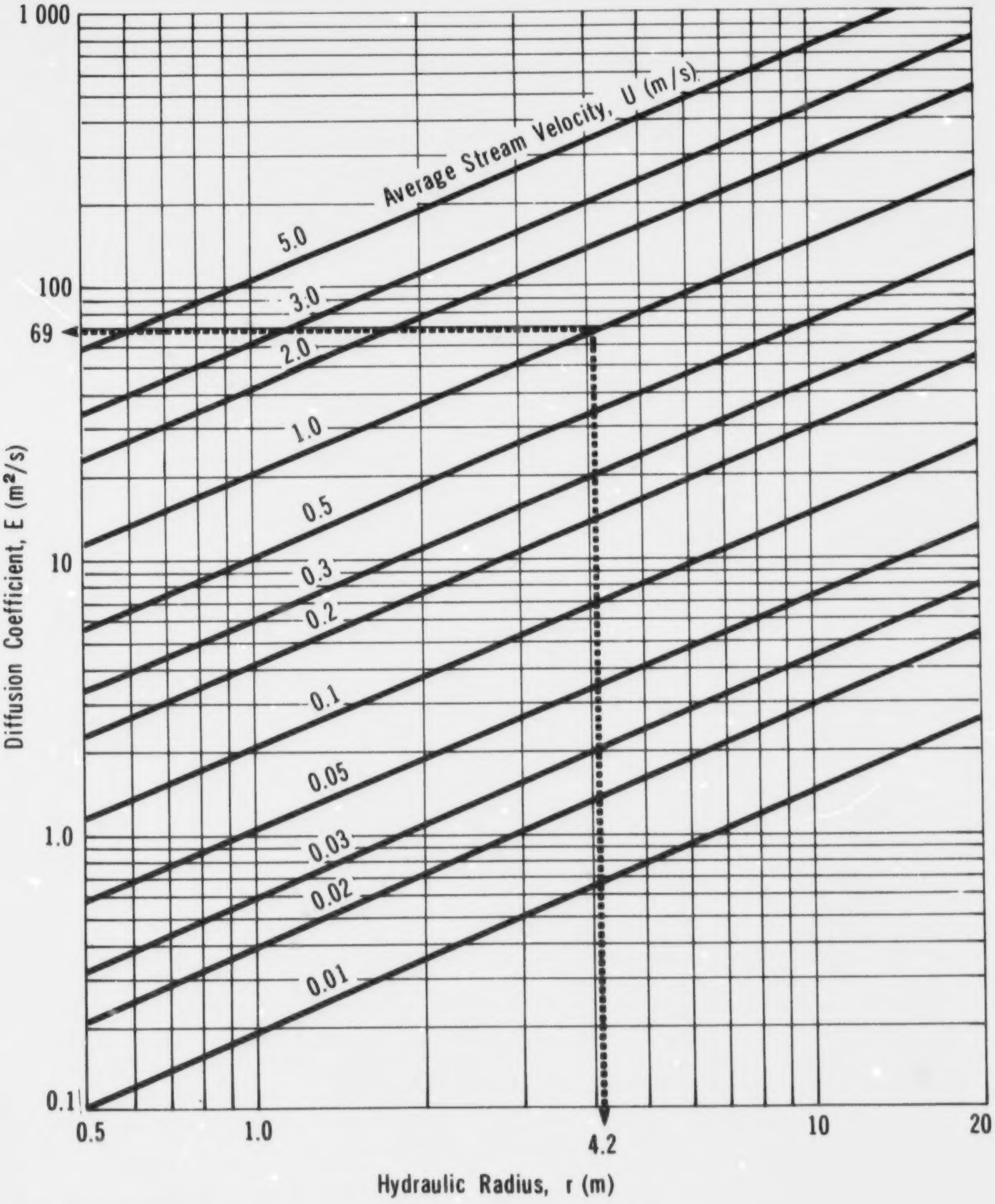
Figure 23: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration

FIGURE 17

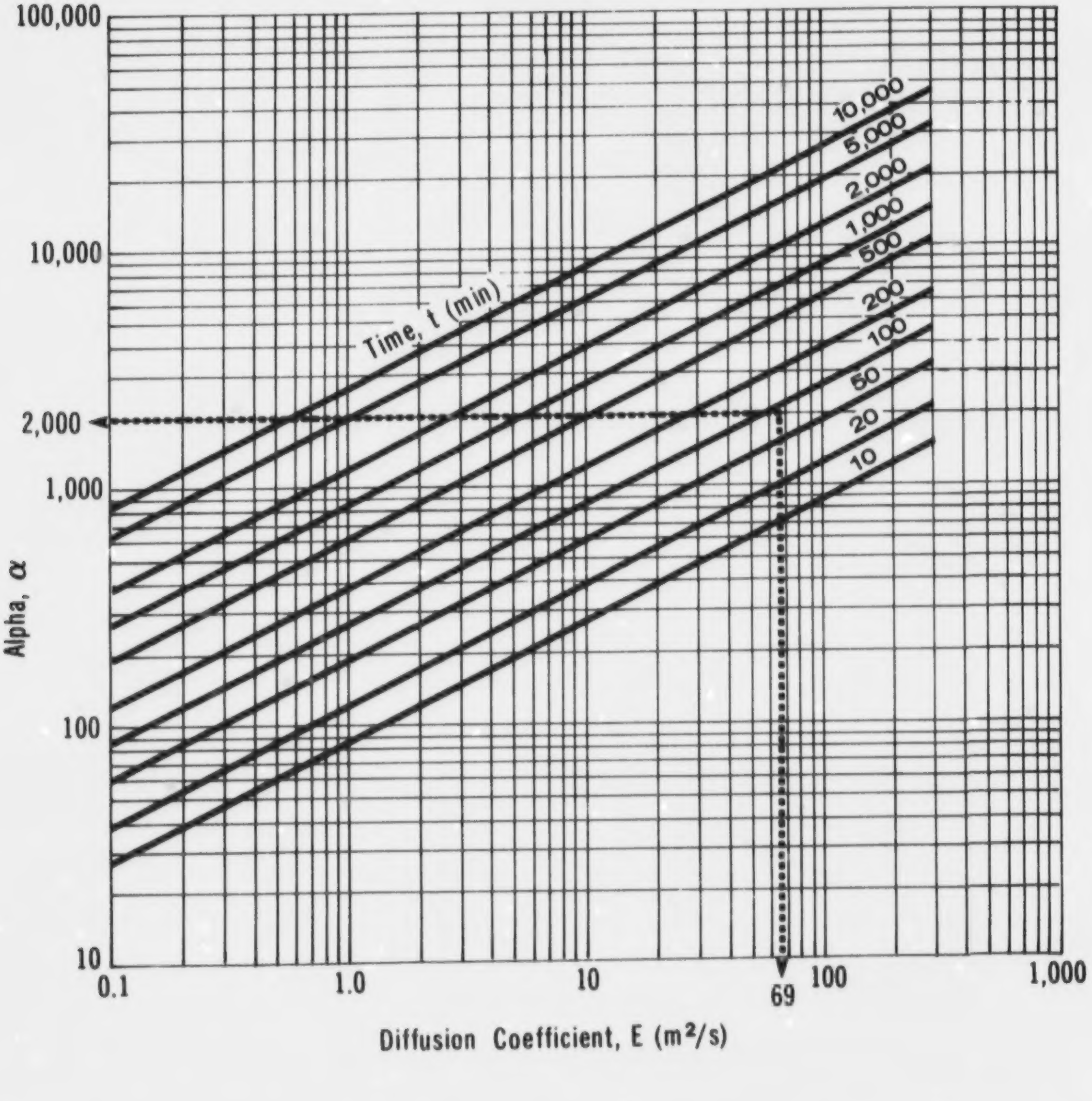
HYDRAULIC RADIUS VS CHANNEL WIDTH



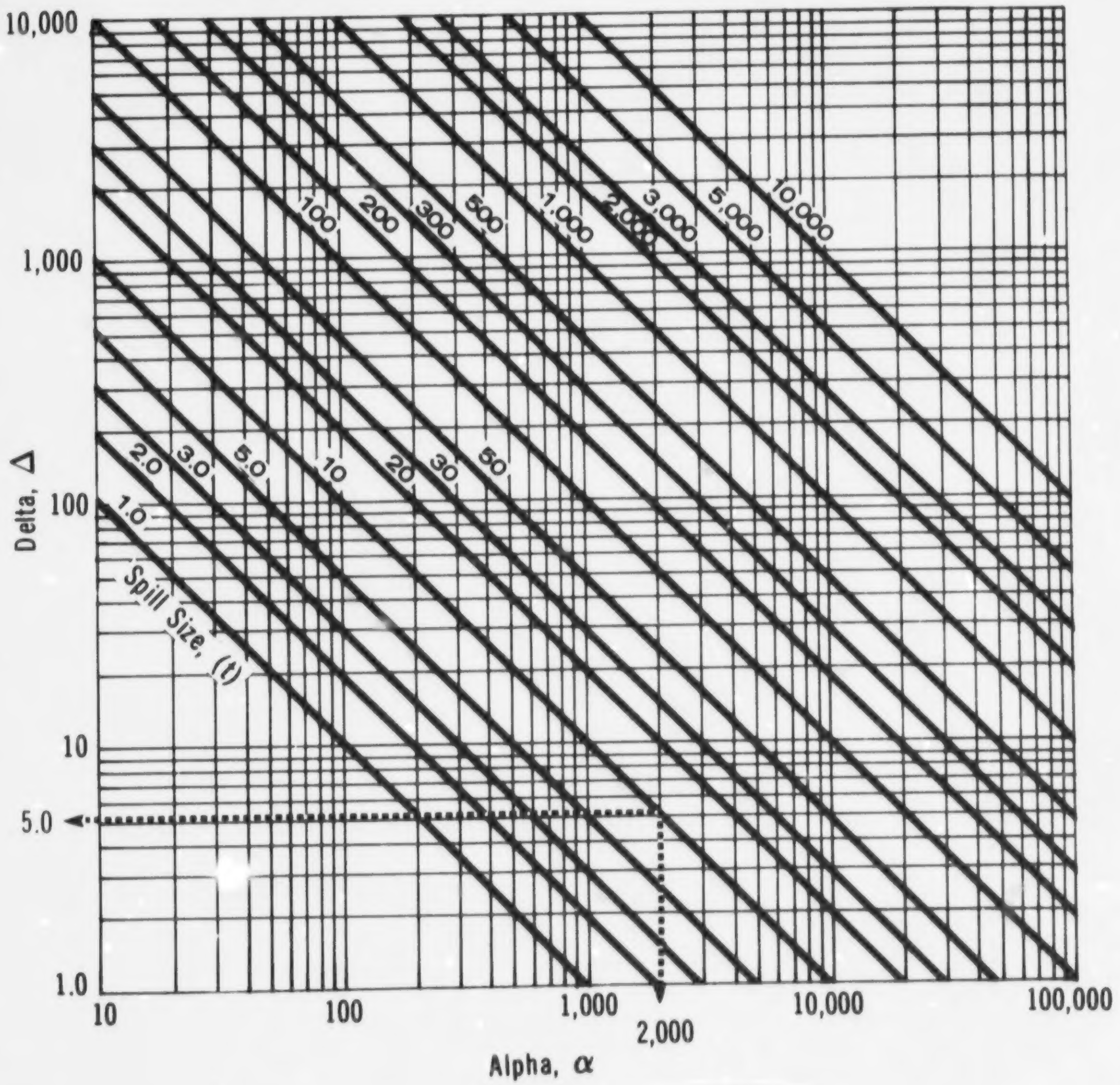
DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT



ALPHA vs DELTA



MAXIMUM CONCENTRATION vs DELTA

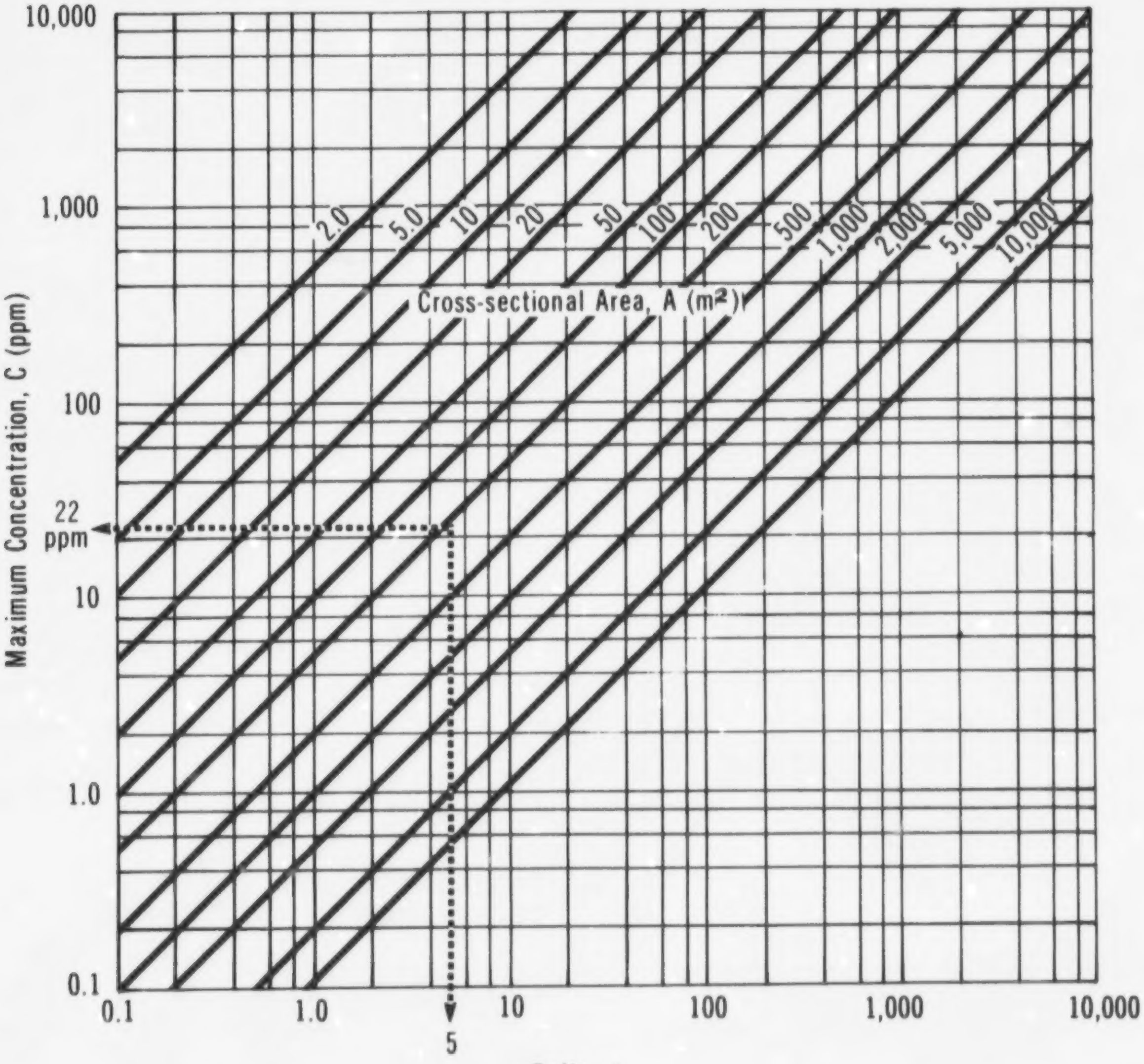


FIGURE 22

VOLUME vs RADIUS

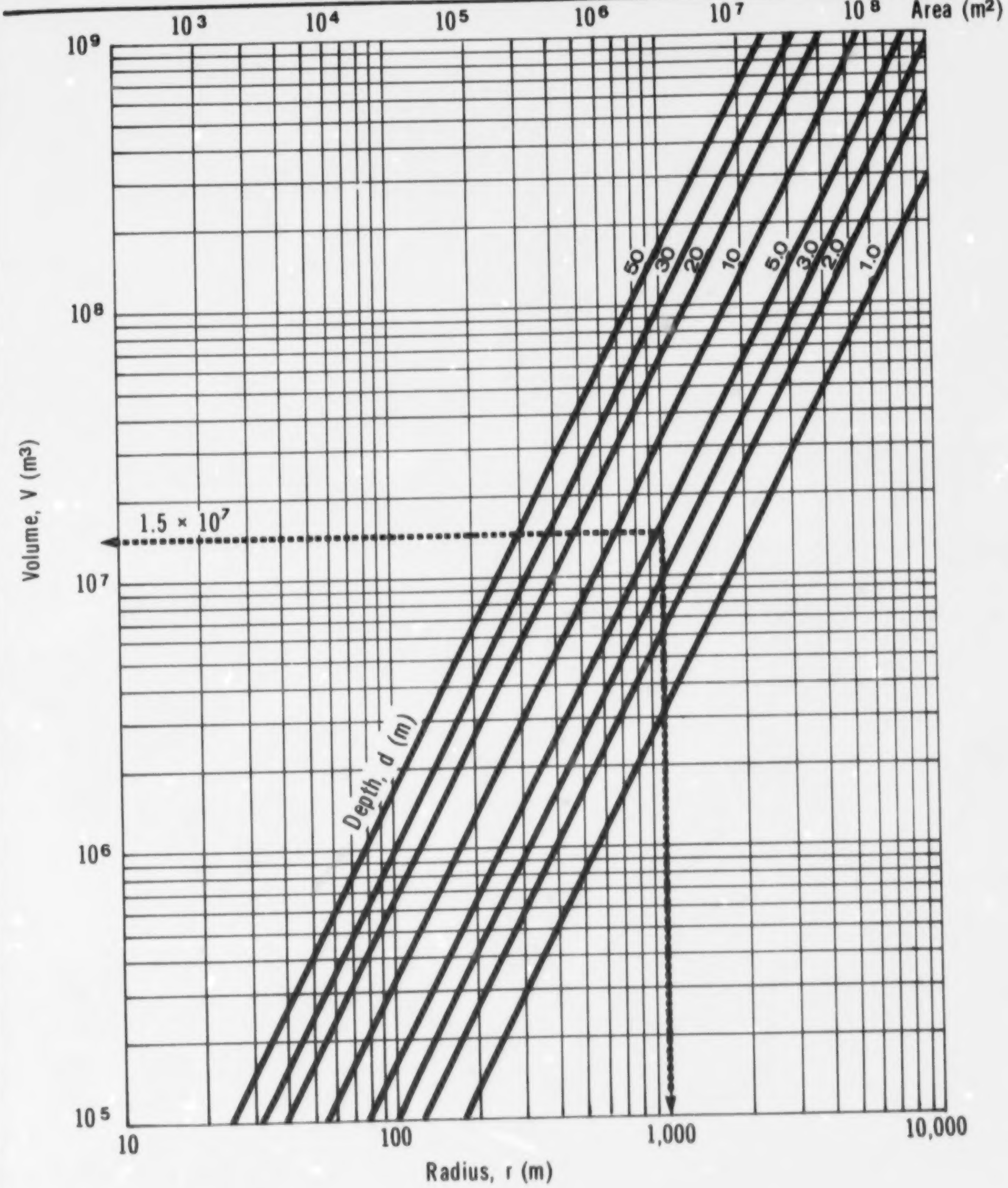
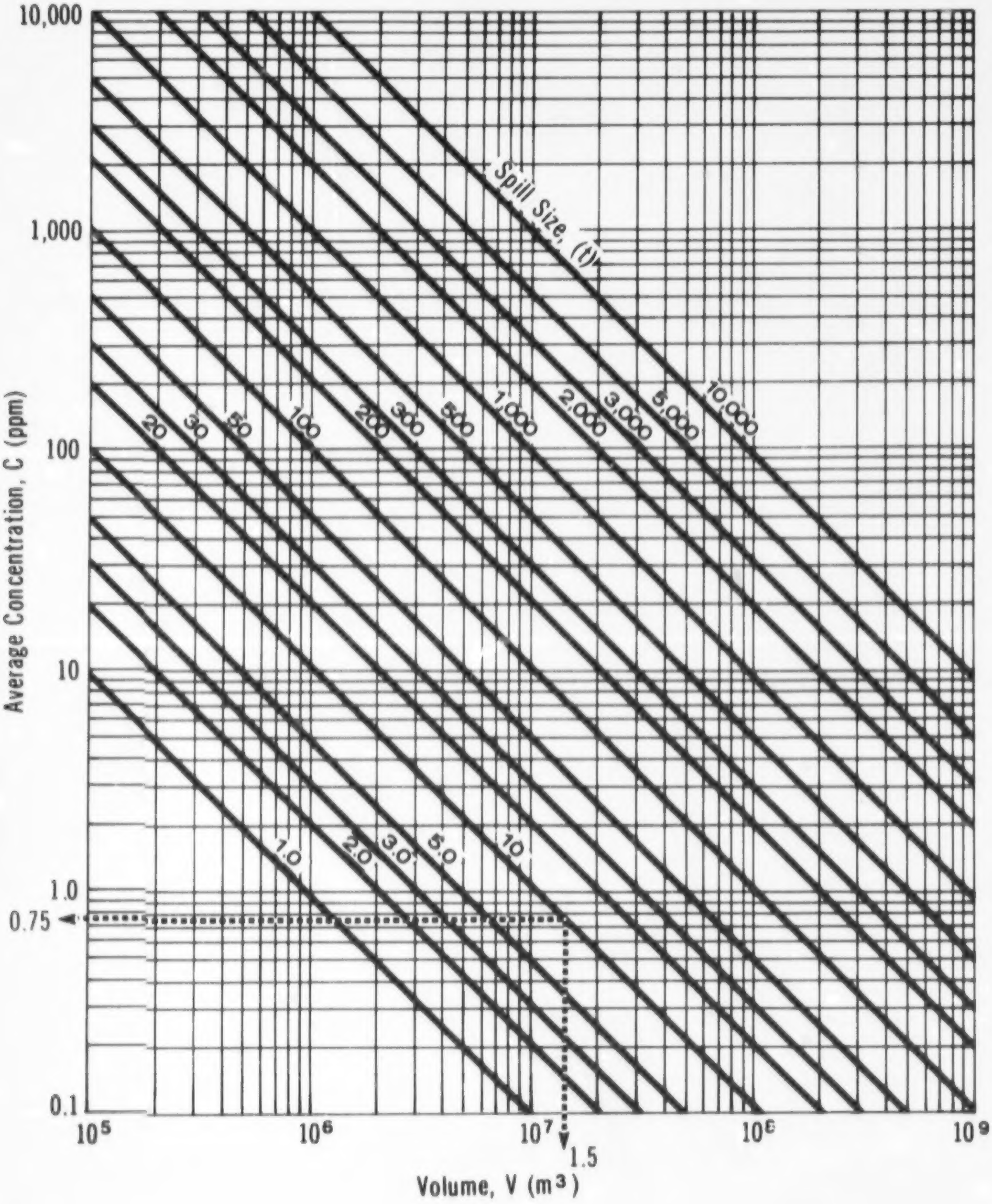


FIGURE 23

AVERAGE CONCENTRATION vs VOLUME



of pollutant (C) can be obtained from Figure 23 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal river. A 20 tonne spill of 50 percent sodium hydroxide solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- $W = 50$ m
- $d = 5$ m
- $U = 1$ m/s
- spill size is 20 tonnes of 50 percent solution, equivalent to 10 tonnes of pure sodium hydroxide
- $X = 5\,000$ m

Step 2: Calculate time to reach point of interest

- Use Figure 16
- With $X = 5\,000$ m and $U = 1$ m/s, $t = 83$ min

Step 3: Calculate hydraulic radius (r)

- Use Figure 17
- With $W = 50$ m and $d = 5$ m, $r = 4.2$ m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 18
- With $r = 4.2$ m and $U = 1$ m/s, $E = 69$ m^2/s

Step 5: Calculate alpha (α)

- Use Figure 19
- With $E = 69$ m^2/s and $t = 83$ min, $\alpha = 2\,000$

Step 6: Calculate delta (Δ)

- Use Figure 20
- With alpha (α) = 2 000 and spill size is 10 tonnes (pure sodium hydroxide), delta (Δ) = 5

Step 7: Compute stream cross-sectional area (A)

$$A = W \times d = 50 \times 5 = 250 \text{ m}^2$$

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 21
- With $\Delta = 5$ and $A = 250 \text{ m}^2$, $C = 22$ ppm

5.4.3.2 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of 50 percent sodium hydroxide solution has occurred in a lake. The point of interest is located on the shore approximately 1 000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- $d = 5$ m
- $r = 1\ 000$ m
- spill size is 10 tonnes (equivalent pure sodium hydroxide)

Step 2: Determine the volume of water available for dilution or

- Use Figure 22
- With $r = 1\ 000$ m, $d = 5$ m, the volume is approximately $1.5 \times 10^7 \text{ m}^3$

Step 3: Determine the average concentration

- Use Figure 23
- With $V = 1.5 \times 10^7 \text{ m}^3$ and spill size of 10 tonnes, the average concentration is 0.75 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 **Introduction.** The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Specific considerations related to the spill of sodium hydroxide onto soil and downward movement toward the groundwater table are presented here.

The forms of sodium hydroxide of interest include solid anhydrous, and 73 and 50 percent solutions. In the case of a solid anhydrous sodium hydroxide spill onto soil, groundwater pollution will occur if precipitation occurs prior to cleanup. Precipitation will dissolve some of the solid (with much heat given off) and create an aqueous solution of sodium hydroxide which then would be able to infiltrate the soil. However, prediction of the concentration and properties of the solution produced would be difficult. A similar circumstance would exist for a spill of 75 percent by weight sodium hydroxide. At ambient temperatures, this material is a highly viscous, gelatinous material; without dilution by precipitation, it would not infiltrate the soil to any significant extent. Precipitation would enhance infiltration. The third form, 50 percent by weight sodium hydroxide, is a liquid which would measurably infiltrate the soil upon being spilled.

Because of this variability, the soil penetration nomograms developed here will consider the extremes: 50 percent sodium hydroxide, and sodium hydroxide diluted to the point where it has transport properties similar to water. As dilution occurs, the speed of movement increases.

During movement through the soil, some ion exchange will occur, with sodium replacing calcium and magnesium ions on clay minerals. However, much of the sodium and virtually all of the hydroxide ion will remain in the aqueous phase and will move downward readily into the soil.

A schematic diagram of a sodium hydroxide spill is shown in Figure 24. Upon reaching the groundwater table, the sodium hydroxide will continue to move in the direction of groundwater flow. Dilution will occur to some degree due to molecular diffusion and dispersion. However, long-term transport is expected.

5.5.2 Equations Describing Sodium Hydroxide Movement in Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Sodium Hydroxide in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

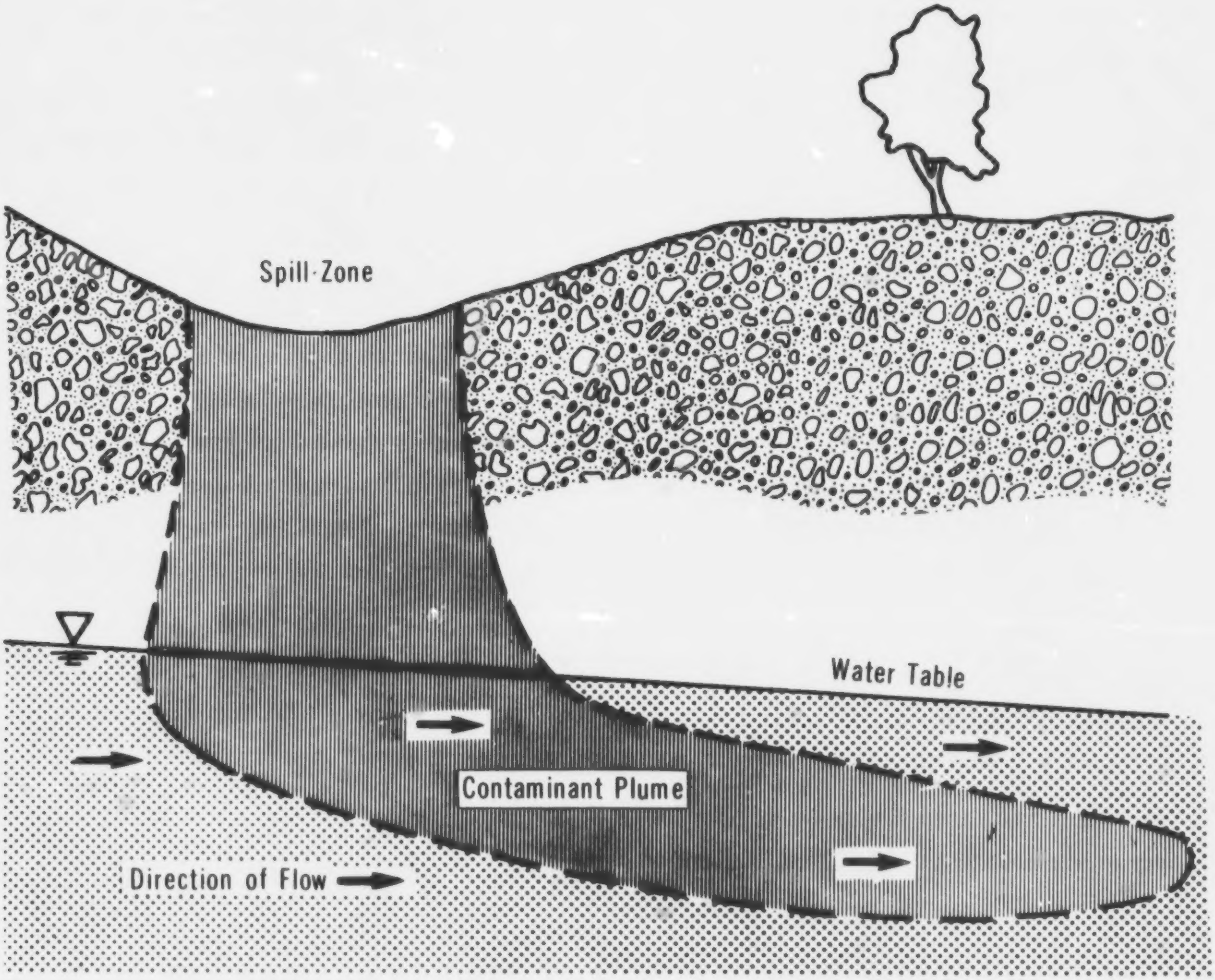
ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa•s)

g = acceleration due to gravity = 9.81 m/s^2

The fluids analyzed here are 50 percent sodium hydroxide solution and water. Only 20°C data were available for 50 percent sodium hydroxide.

SCHEMATIC SOIL TRANSPORT


Spill Zone
Water Table
Contaminant Plume
Direction of Flow

Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

Property	50% Sodium Hydroxide, 20°C	Water, 20°C
Mass density (ρ), kg/m^3	1 500	998
Absolute viscosity (μ), Pa•s	73 x 10^{-3}	1.0 x 10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(2.0 \times 10^5)k$	$(9.8 \times 10^6)k$

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of sodium hydroxide into the unsaturated zone above the groundwater table were prepared for each soil. These present penetration time (t_p) against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

The nomograms include two materials, 50 percent sodium hydroxide and water, the latter representing very dilute sodium hydroxide. The depth of penetration increases with dilution at a given time. A flowchart for the use of the nomograms is presented in Figure 25. The nomograms are presented as Figures 26, 27 and 28.

5.5.6 Sample Calculation. A 20 tonne spill of 50 percent sodium hydroxide solution has been spilled onto a coarse sandy soil. The radius of the spill is 8.6 m. The depth to groundwater is estimated at 3.5 m. What is the depth of penetration 65 minutes after the spill, with the temperature at 20°C?

FIGURE 25

FLOWCHART FOR NOMOGRAM USE

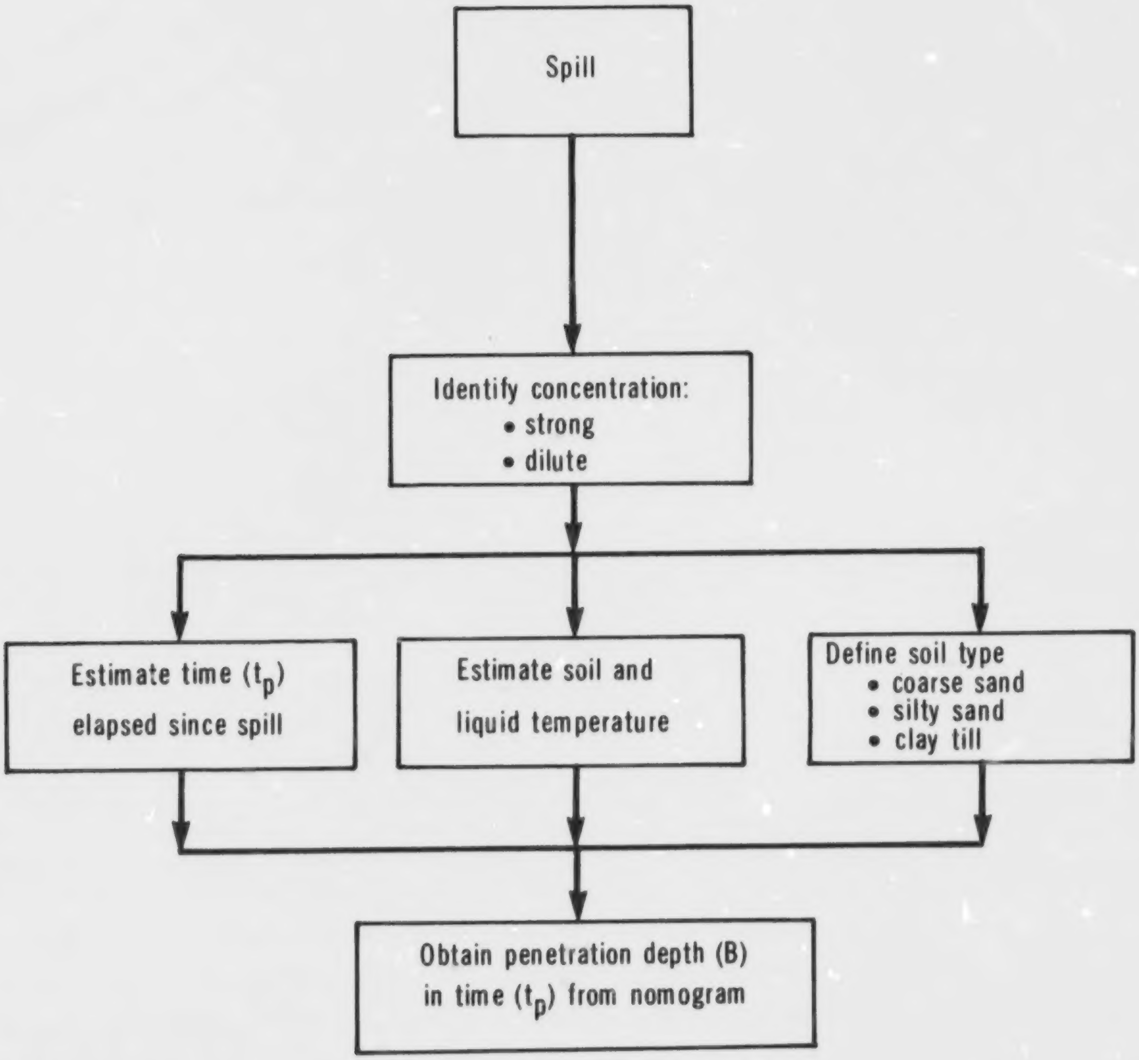
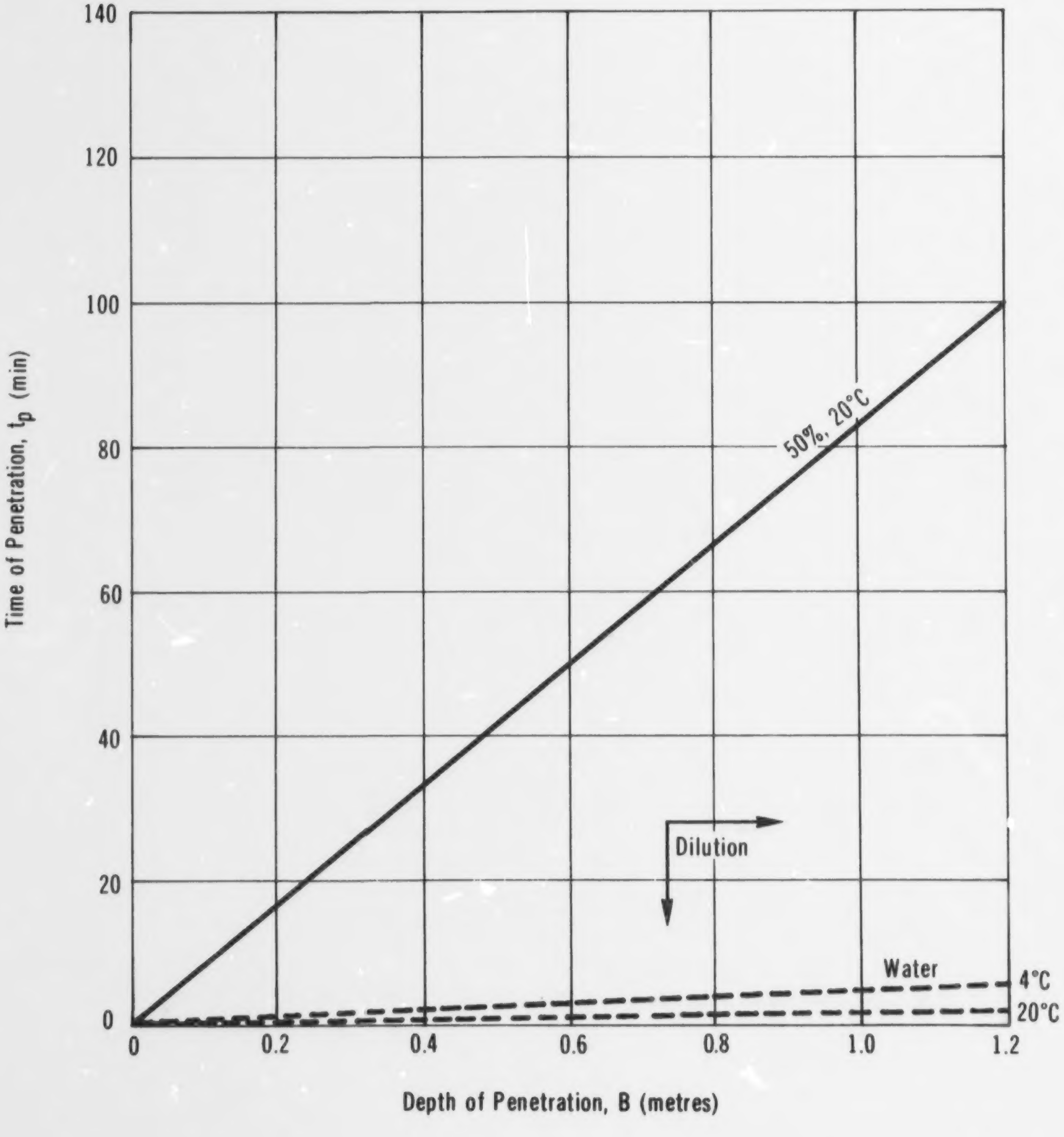

Spill
Identify concentration:
• strong
• dilute
Estimate time (t_p) elapsed since spill
Estimate soil and liquid temperature
Define soil type
• coarse sand
• silty sand
• clay till
Obtain penetration depth (B) in time (t_p) from nomogram

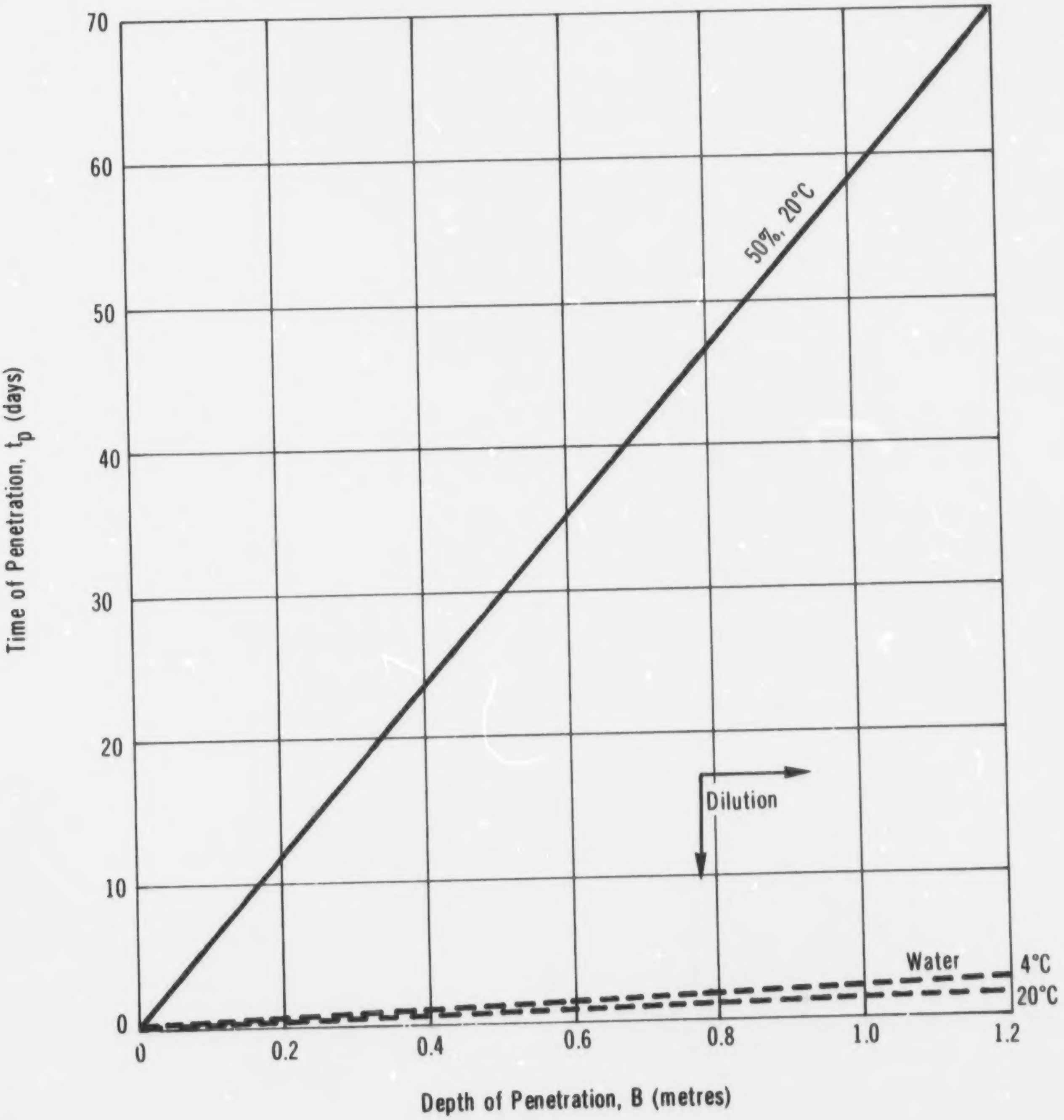
FIGURE 26

SODIUM HYDROXIDE

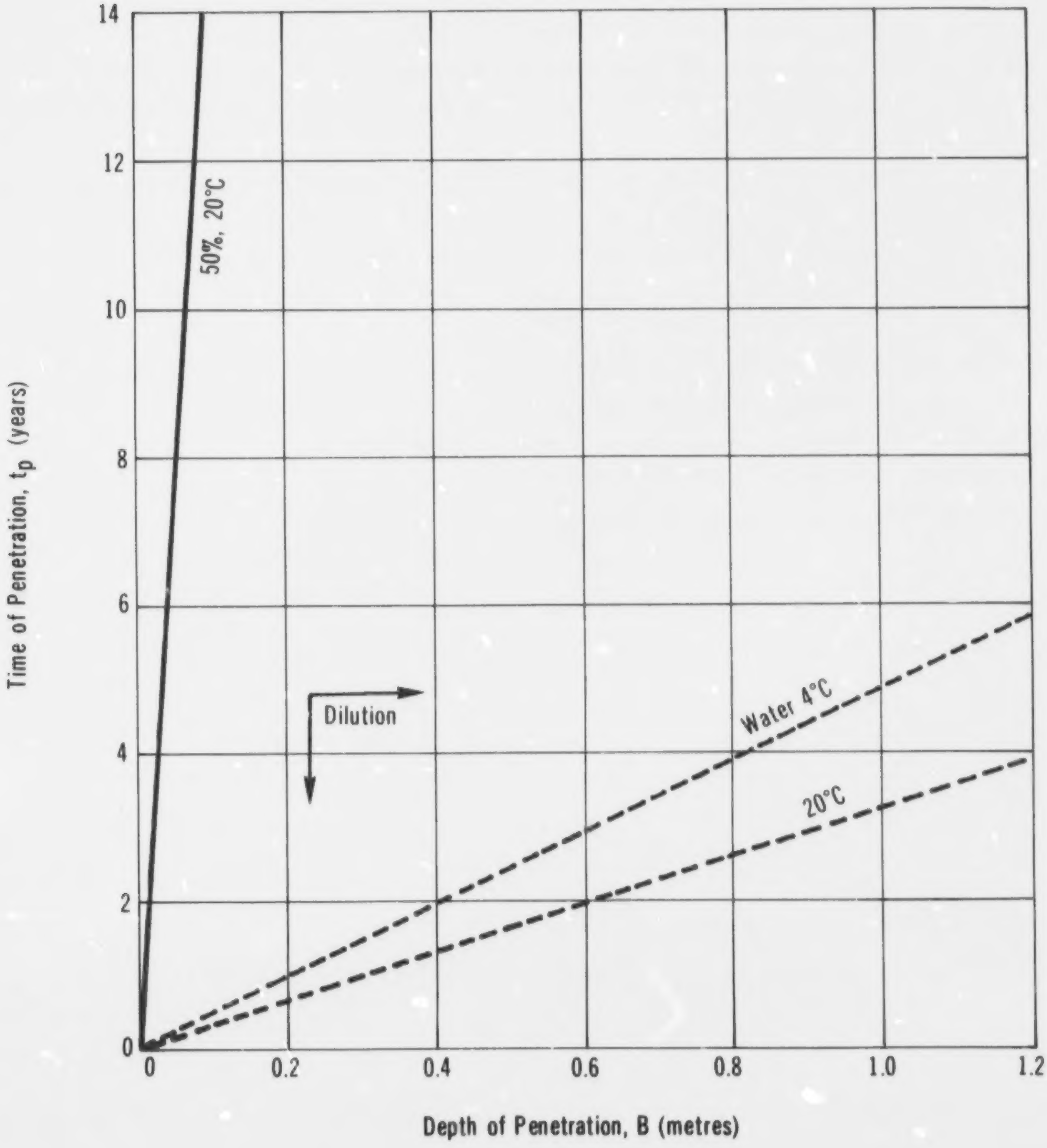
PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND



PENETRATION IN CLAY TILL



Solution

- Use Figure 26
- For t_p = 65 min, the depth of penetration (B) = 0.78 m
- The groundwater table has not been reached in this time. Dilution increases the depth of penetration for a given time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. There is no regulated limit for sodium hydroxide in water in Canada or the United States; however, authorities should be informed when the sodium ion concentration exceeds 20 mg/L (Guidelines/Canadian/Water 1978). Sodium in drinking water may be harmful to persons suffering from cardiac, renal and circulatory diseases; 200 mg (assumed to be mg/L) may be injurious (PB 216658). The pH should not exceed 8.5 for drinking and recreational water (for the latter, this is based on eye irritation properties). Taste of water may be affected by a concentration of 1 to 50 mg/L (WQC 1963). The taste threshold of sodium hydroxide in water is 1-50 mg/L (PB 216658). Excessive alkalinity in irrigation water can be detrimental to certain crops (depending on the physical and chemical properties of the soil). High alkalinities in water can harm stock (PB 216658). A pH of 9.0 is acceptable for livestock (WQC 1963). When caustic alkalinity reaches 50 mg/L, chickens develop diarrhea; at a total alkalinity of 170 mg/L, other animals are similarly affected (PB 216658). The range of recommended threshold values for total alkalinities in water supplies (industrial uses) are: brewing, 50-170 mg/L; carbonated beverages, 50-170 mg/L; food products, 30-250 mg/L; pulp and paper making 45-150 mg/L. Foaming may occur in boilers in the presence of more than 50 mg/L of potassium plus sodium in the water (PB 216658).

6.1.2 Air. No air pollution standards for sodium hydroxide have been promulgated in Canada or in the United States.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Sodium hydroxide has been assigned a TL_m 96 (4-day median lethal toxicity rating) of 10 to 100 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
99	48	Bluegill	TL_m	tap water	WQC 1971
10	tns	Cut-throat trout	safe		WQC 1971

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
50	7 days	Goldfish; bass	safe		WQC 1971
125	96	Mosquito fish	TL_m	turbid water from farm pond	WQC 1971
20 to 40	24	Creek chub	critical range	aerated Detroit River water	WQC 1971
Fish Kill Data					
5	3 to 5 min	Pumpkinseed, eggs and fry	killed		WQC 1971
35	5 days	Cut-throat trout	lethal (min. conc.)	kraft mill waste effluent	WQC 1971
20	5 days	Coho salmon	lethal (min. conc.)	kraft mill waste effluent	WQC 1971
25	24	Brook trout	killed		WQC 1971
100	120	Shiners	killed		WQC 1971
100	3 to 120	Goldfish; bass	killed		WQC 1971
Microfauna					
156	tns	Daphnia	lethal, immobilization	Lake Erie water, pH 9.1 to 9.5	WQC 1971
Insects					
125 to 1 000	tns	Various insect larvae	lethal		WQC 1971
400	tns	Water beetles	stimulate movement		WQC 1971
Invertebrates					
150	24	Vector snails	lethal	27°C	Gohar 1961
4×10^{-6} M	48	Planarian worm	lethal	pH 7.8, distilled	WQC 1971

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Invertebrates					
10	not stated	Caspian Sea shrimp	stimulating effect on respiration		Nadzhafova 1979
90	4.5	Oysters	lethal	circulating	WQC 1971
30 to 100	48	Shrimp	LC_{50}	aerated	Portman 1970
33 to 100	48	Starfish	LC_{50}	aerated	Portman 1970
330 to 1 000	48	Marine mussel	LC_{50}	aerated	Portman 1970

6.3 Aquatic Studies

The upper pH limit tolerated by most freshwater fish is 8.4; the pH must generally be greater than 9 before the aqueous environment becomes lethal for fully developed fish. Freshwater algae are destroyed above pH 8.5. In brackish waters, oyster larvae have been injured at pH 9 and died at pH 9.1 in a few hours. The upper pH limit for crabs is 10.2. Concentrations of 500-1 000 mg/L of sodium (when present as the chloride or nitrate) have been found to be toxic to fish in saltwaters. The US EPA acceptable range for pH is 5 to 9 for domestic water supplies; 6.5 to 9.0 for freshwater aquatic life; and 6.5 to 8.5 for marine aquatic life (Hooker PIM; PB 216658). Concentrations of 20 to 100 mg/L of sodium hydroxide in water have been found to kill salmon, trout, carp and crayfish (WQC 1971). The lethal threshold extends from pH 9.2 for brook trout to pH 10.8 for carp (Loub 1975), to pH 10.9 for goldfish and to pH 10.5 for bluegills (EPA 440/9-75-009; Hooker PIM).

6.4 Effect Studies

The damaging effects are mostly a consequence of the increase in pH (EPA 440/9-75-009). Fish develop burns on the outer skin of the gills, with strong slime formation. They die by suffocation due to slow destruction of their respiratory organ.

6.5 Degradation

The pH effect of hydroxide ion is naturally reduced by the absorption of atmospheric carbon dioxide. This reduction is also effected by dilution with water and by the natural acidity of a given water body (EPA 440/9-75-009). Strictly speaking, there is no degradation of sodium hydroxide in waters, only loss by absorption or through chemical neutralization.

7 HUMAN HEALTH

Toxicological information in the literature on human health effects of sodium hydroxide emphasizes the corrosive effects on skin, eyes, and mucous membranes. The ingestion of sodium hydroxide can be fatal unless treatment is immediate (Meyer 1977). The irritating nature of the aerosol on the mucous membranes is presumed to be adequate warning to maintain air concentrations at tolerable levels. Animal research has been largely confined to eye and skin effects and to ingestion toxicity, although some chronic inhalation studies have been cited. Cancer has been observed as sequelae following severe tissue damage, and has been attributed to the tissue damage itself rather than to the chemical exposure.

No information was found in the literature on the effects of sodium hydroxide exposure on reproduction. Limited information on mutagenicity has been published. Since 1976, no research projects on the toxicology of sodium hydroxide have been reported in the TOX TIPS (a summary of current research activity).

The toxicological data summarized here have been extracted from published papers and reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for sodium hydroxide are designed to protect the respiratory tract from irritation. Canadian provincial guidelines are generally similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
PEL (8 h)	USA-OSHA	2.0 mg/m^3 (water aerosol)	NIOSH Guide 1978; PB 216658
Short-term Exposure Limits (STEL)			
Permissible Exposure Limit, 15 min ceiling	USA-NIOSH	2 mg/m^3 (water aerosol)	NIOSH Guide 1978

Guideline (Time)	Origin	Recommended Level	Reference
Ceiling Limit	USA-ACGIH	2 mg/m^3 (water aerosol)	Doc. TLV 1981
Other Human Toxicities			
IDLH	USA-NIOSH	200 mg/m^3 (water aerosol)	NIOSH Guide 1978

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
25 to 50% (3 min)	Sensation of irritation	Proctor 1978
4% (Several hours)	Sensation of irritation	Proctor 1978
20 µL 1 N NaOH applied 1 to 3x at 30 min intervals (60 min)	Progressive dissolution of surface skin cells (horny layer) to edema and total destruction of epidermis	Nagao et al. 1972. IN NIOSH 1975
SPECIES: Rabbit		
50 mg (24 h)	Severe	RTECS 1979
SPECIES: Rat		
50% (1 min) Followed by wiping, neutralization, and washing	Edema, ulceration of skin with formation of thick sloughs	TDB (on-line) 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
180 mg/m^3 (3 min)	Slight prickling and watering sensation, lasting for 24 h	Cooper 1979
3 mg/m^3 (11 min)	Slight prickling behind eyelids	Cooper 1979
SPECIES: Monkey		
1% Solution (24 h)	Severe	RTECS 1979
SPECIES: Rabbit		
1% Solution	Severe	RTECS 1979
1 mg (24 h)	Severe	RTECS 1979
50 µg (24 h)	Severe	RTECS 1979

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Odourless (CHRIS 1978).

7.3.2 Taste.

Taste Characteristic: Bitter (AAR 1981).

Parameter	Media	Concentration	Reference
Detection Threshold	Water	0.08 mg/L	ASTM 1980
Lower Taste Threshold	-	1 ppm	OHM-TADS 1981
Upper Taste Threshold	-	50 ppm	OHM-TADS 1981
Taste Threshold	Water	1-50 mg/L	PB 216658

7.4 Long-term Studies

7.4.1. Inhalation. "Inhalation of sodium hydroxide has received little attention. It may be assumed that the irritating nature of the aerosol on mucous membranes has prompted the maintenance of airborne concentrations of sodium hydroxide at tolerable levels" (NIOSH 1975).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Man		
35 mg/m^3 (11 min)	(With goggles). Capable of work. Mouth breathing induced coughing	Cooper 1979
25 mg/m^3 (11 min)	(With goggles). Slight prickling in upper nasal passages, irritation not severe. Capable of work	Cooper 1979
10 to 2 mg/m^3 (5 min)	Characteristic odour. Slight watering of eyes and nose	Cooper 1979
3 mg/m^3 (11 min)	Slight prickling behind eyelids	Cooper 1979
SPECIES: Rat		
3,200 μg/L (1.5 h)	Respiratory distress in 12	Zwicker 1979
865 μg/L (2 h) 35% NaOH/65% Na_2CO_3	Of 12 adults, 6 had acute laryngitis; severity rated very slight	Zwicker 1979
750 μg/L (2 h) NaOH	Of 24 juveniles, 22 had acute laryngitis; severity rated slight	Zwicker 1979
Chronic Exposures		
SPECIES: Human		
0 to 1.5 mg/m^3 (Occupational)	No significant contribution to eventual cause of death. During working lifetime, medical aid sought more for skin contact than for eye contact, and more for eye contact than for inhalation	Ott 1977

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
Aerosol from 40% solution, 80% of droplets <1 µm diameter (30 min, 2x/d for 75 d)	Irregularities in pulmonary tissue - cell proliferation, congestion. Undescribed, isolated tumours (3 of 10 animals). Thickened lymph-adenoidal tissue penetrating muscle under epithelium. Proliferated lymph-adenoidal tissue adhering to bronchial lumen. Isolated areas of lung parenchyma fused together. Bronchial pneumonia	Dluhos et al. 1969. IN NIOSH 1975
Aerosol from 40% solution, followed by aerosol from 8% solution of NH_4Cl (30 min, 2x/d for 75 d)	Death (3 of 10) after 3 weeks. Discoloration of lungs. More extensive damage than NaOH exposure only. Interstices infiltrated by lymphocytes, plasma cells, hystiocytes	Dluhos et al. IN NIOSH 1975
Aerosol from 40% solution. Simultaneous exposure to quartz dust (2x/wk)	Death within 1 month due to bronchial pneumonia	Vyskocil et al. IN NIOSH 1975
Aerosol from 20% solution. Simultaneous exposure to quartz dust	Septa dilated and cracked. Bronchi dilated, their epithelial cover thinned, and infiltration of submucous membrane tissue by round cells	Vyskocil et al. IN NIOSH 1975
Aerosol from 10% solution. Simultaneous exposure to quartz dust	Little change	Vyskocil et al. IN NIOSH 1975
Aerosol from 5% solution	Dilation of bronchi, slight degeneration of mucous membrane, thickened lymph-adenoidal tissue surrounding bronchi	Vyskocil et al. IN NIOSH 1975

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
5 g	LD_{50}	Dreisbach 1980
1.95 g	Death	OHM-TADS 1981
SPECIES: Rabbit		
500 mg/kg	LD_{LO}	AAR 1981; RTECS 1979

7.4.3 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
40 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutation Data.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Cultured Cells		
20 µL	Chromosomal aberrations	RTECS (on-line) 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated. In general, sodium hydroxide is corrosive to all tissues.

7.5.1 Inhalation.

1. Sneezing and coughing.
2. Irritation of eyes, nose, throat and upper respiratory tract.
3. Burning and redness of eyes, nose (NIOSH 1975).
4. Burning and dryness of throat (NIOSH 1975)
5. Ulceration of nasal passages (TDB (on-line) 1981).
6. Inflammation of the lungs (ITII 1981).
7. Pneumonitis (Proctor 1978).
8. Pulmonary edema (Doull 1980).
9. Shock (Doull 1980).

7.5.2 Ingestion.

1. Burning pain extending down the esophagus to the stomach.
2. Mucous membranes are white in colour, later turn brown.
3. Profuse salivation (TDB (on-line) 1981).
4. Contaminated areas of lips, chin, tongue, and pharynx edematous and covered with exudate (TDB (on-line) 1981).
5. Severe pain in swallowing.
6. Edema of glottis (Lefèvre 1980).
7. Vomiting of large pieces of mucosa.
8. Stomach cramps.
9. Rapid breathing.
10. Rapid and feeble pulse. Shock.
11. Diarrhea, possibly blood-stained.
12. Severe sub-sternal pain with fever (TDB (on-line) 1981).
13. Esophageal stenosis or antropyloric stenosis (NIOSH 1975).
14. Pneumonia, aspiration pneumonitis, or asphyxia from glottic edema may cause death (TDB (on-line) 1981).
15. Cardiovascular collapse and coma (ITII 1981).
16. Improvement may occur for 2 to 4 days. Then abdominal pain, rapid fall in blood pressure due to gastric or esophageal perforation (TDB (on-line) 1981).
17. Squamous cell carcinoma of the esophagus after latent periods of 12 to 42 years. This is considered to be a sequela of tissue destruction rather than the carcinogenic effect of sodium hydroxide (Proctor 1978).
18. Prostration
19. Constrictive scarring may result (Merck 1983)

7.5.3 Skin Contact.

1. There is not necessarily an immediate sensation of irritation or pain (NIOSH 1975).
2. Primary irritant dermatitis.
3. Multiple small burns with temporary loss of hair.
4. Deterioration of keratin material.
5. Intracellular edema.
6. Severe burns, corrosion of tissue, deep ulcerations and ultimate scarring.

7.5.4 Eye Contact.

1. Irritation.
2. Conjunctivitis, corneal burns.
3. Photophobia (NIOSH 1975).
4. Disintegration and sloughing of conjunctival and corneal epithelium (Proctor 1978).
5. Corneal edema, ulceration, and opacification.
6. Symblepharon (Proctor 1978).
7. Overgrowth of the cornea by a vascularized membrane (Proctor 1978).
8. Permanent corneal opacification.
9. Severe damage.

7.6 Human Toxicity to Decay or Combustion Products

Sodium hydroxide solutions may produce hydrogen gas during reaction with amphoteric metals.

7.6.1 Hydrogen. Hydrogen is a colourless, tasteless, odourless gas which, when mixed with air, forms explosive mixtures.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Water	x									x	x		Violent boiling	Bretherick 1979
SPECIFIC CHEMICALS														
Acetaldehyde					x								Polymerizes violently	NFPA 1978
Acetic Acid	x								x				Pressure rise in closed container with glacial acetic acid	NFPA 1978
Acetic Anhydride	x								x				Pressure rise in closed container	NFPA 1978
Acrolein					x								Polymerizes violently	NFPA 1978
Acrylonitrile					x								Polymerizes violently with concentrated caustic	NFPA 1978
Allyl Alcohol					x								Polymerizes violently; reaction produced allyl alcohol which exploded	NFPA 1978
Allyl Chloride					x									NFPA 1978

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Aluminum				x									Produces explosive hydrogen	Bretherick 1979
Bromine			x										If not mixed	Bretherick 1979
Chlorine Trifluoride										x			With mixture of nitric acid, potassium and silver salts	NFPA 1978
Chlorohydrin	x								x				In closed container	NFPA 1978
4-Chloro-2 Methylphenol			x										After mixing for several hours	Bretherick 1979
Chloronitrotoluenes	x		x						x				Possible explosion in closed container	NFPA 1978
Chlorosulphonic Acid	x								x				In a closed container	NFPA 1978
Cinnamaldehyde	x	x											Rags soaked in both ignited in a bin	Bretherick 1979
Cyanogen Azide			x										Detonated by alkalies	Bretherick 1979
1,2-Dichloroethylene				x									May form mono- or dichloroacetylene which are spontaneously flammable	NFPA 1978

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Diborane	x		x										With octanal oxime, very exothermic and may explode	Bretherick 1979
Ethylene Cyanohydrin	x								x				In a closed container	NFPA 1978
Glyoxal	x								x				In a closed container	NFPA 1978
Hydrochloric Acid	x								x		x		In a closed container with 36% HCl	NFPA 1978
Hydrofluoric Acid	x								x		x		With 48.7% HF in a closed container	NFPA 1978
Hydroquinone	x					x							Pumped into tank by error caused heat evolution and overflow	NFPA 1978
Maleic Anhydride			x			x							Explosive decomposition	NFPA 1978
Nitric Acid	x								x				With 70% HNO_3 in closed container	NFPA 1978
Nitro Benzene			x										Causes detonation	Bretherick 1979
Nitro Ethane			x										Causes detonation	NFPA 1978

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitro Methane			x										Causes detonation	NFPA 1978
Nitro Propane			x										Causes detonation	NFPA 1978
Oleum	x								x				In a closed container	NFPA 1978
Pentol			x										Upon contact	NFPA 1978
Pentachlorophenol			x					x						Bretherick 1979
Phosphorus		x						x					When boiled yields phosphine gas	Bretherick 1979
Phosphorus Pentoxide											x		Violent reaction when heat initiated	NFPA 1978
β-Propiolactone	x								x				In closed container	NFPA 1978
Sodium Tetrahydroborate			x						x				Liberates hydrogen explosively	Bretherick 1979
Sulphuric Acid	x								x				With 96% H_2SO_4 in closed container	NFPA 1978
Tetrahydrofuran			x										On contact	NFPA 1978

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
1,2,4,5-Tetrachlorobenzene	x		x						x				Reaction may get out of control, pressurizing container and exploding	Bretherick 1979
1,1,1-Trichloroethanol			x										Forms explosive chlorohydroxyacetylene	Bretherick 1979
Trichloroethylene		x	x										Forms mixtures of dichloroacetylene which are explosive	NFPA 1978
Trichloronitromethane			x										Can cause detonation	Bretherick 1979
Zinc		x											With powdered zinc	Bretherick 1979
Zirconium			x										Explosive when heated	Bretherick 1979
CHEMICAL GROUPS														
Alkali and Alkaline Earth Metals	x			x									Yields hydrogen	EPA 600/2-80-076
Epoxides	x				x									EPA 600/2-80-076
Esters	x												Hydrolysis to the associated salt and alcohol	EPA 600/2-80-076

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Explosives	x		x										Reaction can generate enough heat to detonate explosive	EPA 600/ 2-80-076
Halogenated Organics - Aliphatic	x			x									Yields flammable olefins and acetylene	EPA 600/ 2-80-076
Isocyanates	x				x	x							Monoisocyanates decompose. Diisocyanates polymerize	EPA 600/ 2-80-076
Ketones	x										x		Self-condensation of the ketone	EPA 600/ 2-80-076
Nitroalkanes and Nitroaromatics			x										Forms salts that are explosive when dry	EPA 600/ 2-80-076
Non-oxidizing Mineral Acids	x								x		x			EPA 600/ 2-80-076
Organic Acids	x								x					EPA 600/ 2-80-076
Organophosphates	x													EPA 600/ 2-80-076
Oxidizing Mineral Acids	x								x		x			EPA 600/ 2-80-076

8.1 Compatibility of Sodium Hydroxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Polymerizable Compounds	x				x									EPA 600/ 2-80-076
Water-reactive Substances	x		x	x				x			x		May also result in unstable mixtures	EPA 600/ 2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Sodium hydroxide is a noncombustible material. However, the solid form in contact with moisture or water may generate sufficient heat to ignite combustible materials. Reaction with amphoteric metals can generate hydrogen gas which may form an explosive mixture with air (NFPA 1978; Kirk-Othmer 1978). Solid sodium hydroxide, when heated to temperatures greater than 318°C, will flow to low ground. When hot or in the molten state, it can react violently with water, causing splattering and releasing an irritating mist. Overheating of sodium hydroxide (solution or molten) in metal storage container accelerates corrosion (Hooker PIM; GE 1977).

9.1.2 Fire Extinguishing Agents. Sodium hydroxide will neither burn nor support combustion. If involved in a fire, use water spray to cool containers, to help prevent rupture or corrosive attack (ERG 1980; GE 1977; Hooker MSDS 1976). Move containers from fire area if this can be done without risk (ERG 1980). Use water or other medium suitable to surround fire (Hooker PIM).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact and inhalation of dust and mist (Hooker PIM 1980).

The following absorbent materials have been tested and recommended for vapour suppression and/or containment of 50 percent sodium hydroxide solutions: perlite and Cellosize WP3H (hydroxyethyl cellulose) (Braley 1980); sand or earth (Hooker PIM).

9.1.3.2 Spills on land. When spilled in solid form, sodium hydroxide should be promptly shovelled into steel drums for recovery or disposal (avoid dusting). Delay in response may allow absorption of moisture from the atmosphere and may increase the difficulties of cleanup (GE 1977; Hooker PIM).

When spilled in solution form, contain if possible, soak up with sand or earth, and shovel into steel containers for disposal (Hooker PIM; ERG 1980). Vermiculite or other inert absorbent material should also be considered (Hooker DS 1979). Depending on the size of the spill, pick up spilled material with vacuum equipment (alkali-resistant) for disposal (GE 1977). Application of fly ash or cement powder to absorb the residual liquid should also be considered (EPA 670/2-75-042). Sorbents such as activated carbon, amberlite and USM may also be used (CG-D-38-76).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. After completion of initial spill actions, neutralize the contaminated area with dilute acid, preferably acetic acid, to remove final traces of sodium hydroxide ion. Sodium bicarbonate may then be used to partially neutralize any residuals (GE 1977).

9.1.4.2 Spills in water. Sodium dihydrogen phosphate is recommended as an in situ neutralizing agent to avoid overdosing, resulting in too great a pH decrease (CG-D-16-77). Carbon dioxide and sodium bicarbonate have similar advantages; zeolite may also be considered for small spills (CG-D-38-76).

9.1.4.3 General. For treatment of contaminated water, gravity separation of solids, followed by neutralization using acetic or dilute sulphuric or hydrochloric acid, is recommended (EPA 600/2-77-227). If other solids form, gravity separation may be required again.

9.1.5 Disposal. Waste sodium hydroxide must never be discharged directly into sewers or surface waters. Following neutralization, either at the spill site or at a waste management facility, the resultant sludge, if any, can be disposed of to secure landfill.

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be sodium hydroxide:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with sodium hydroxide or its solutions (NIOSH/OSHA 1981).

- Dust- and splash-proof safety goggles are also recommended where there is any possibility of sodium hydroxide or its solutions contacting the eyes (NIOSH/OSHA 1981). Chemical safety goggles should also be considered for eye protection (GE 1977).
- PVA is not recommended for gloves (OHM-TADS 1981).
- The following chemical suit materials are recommended for protection against sodium hydroxide (EE-20): butyl, neoprene and cloropel (excellent resistance), and PVC (good resistance).
- Non-impervious clothing which becomes contaminated with sodium hydroxide should be removed immediately and not reworn until the sodium hydroxide is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash stations and safety showers must be immediately available in areas of use and potential spill situations (GE 1977).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where sodium hydroxide is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 2 mg/m^3
Particulate Concentration 100 mg/m^3 or less	A high-efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet or hood.
	Any self-contained breathing apparatus with a full facepiece.
200 mg/m^3 or less	A powered air-purifying respirator with a full facepiece and a high-efficiency particulate filter.
	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode, or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 200 mg/m^3** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-con-

Condition	Minimum Respiratory Protection* Required Above 2 mg/m^3
	tained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator with a full facepiece, except single-use. Any escape self-contained breathing apparatus with a full facepiece.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of sodium hydroxide; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 200 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.7 Special Precautions. Store in well-sealed containers which are protected from physical damage; avoid handling conditions which can lead to spills or mist formation (GE 1977). Store in a dry place to protect against moisture and water. Separate from acids, metals, explosives, organic peroxides and easily ignitable materials (NFPA 1978). Have abundant running water available where stored, unloaded or handled. Drains must have retention basins for pH adjustment and neutralization of spilled materials and flushings before discharge (GE 1977).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study:

Leak Plugging	Plug N'Dike™
Transfer Systems Centrifugal Pumps	Bell & Gossett
Temporary Storage Bag System	Portable Collection
Treating Agents	Hazorb (sorbent)
Gelling Agent	Spill/Clean

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included; the number of experiences is thus not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 **Tank Car Derailment** (Personal Communication EPS 1982; HMIR 1981)

A tank car derailment which resulted from a broken rail caused eight tank cars containing 50 percent aqueous sodium hydroxide to rupture. More than 590 000 L of the liquid were spilled in the area.

Response crews constructed earthen dykes on both sides of the railway track and used vacuum trucks to remove the product that collected behind the dykes and in the culverts. Within 10 days, approximately 135 000 L of spilled product were recovered. The remaining spilled material was expected to enter the porous glacial till at the site and not spread for a length of time. No excavation or neutralization occurred during cleanup. It was considered that any contamination would probably be confined to an aquifer approximately 4 m deep. Most wells in the area draw water from an aquifer at a depth of 10 m. Monitoring of private dwelling wells revealed no environmental effects; the pH and sodium concentration in the water was normal for the area.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analyses of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites, and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Sodium Hydroxide in Air

11.1.1 Titration (NIOSH 1977). This method is useful for concentrations of sodium hydroxide from 1 to 4 mg/m^3 (0.6 to 2.4 ppm) in air. Total hydroxide content, which is considered to be the harmful agent in sodium hydroxide exposure, is measured rather than sodium content.

A measured volume of air is passed through 15 mL of approximately 7 x 10^{-3} N hydrochloric acid in a fritted glass bubbler. A sample size of 350 L of air is recommended. The sample is diluted to 100 mL. It is titrated with 0.1 N sodium hydroxide using a microburet assembly for electrometric titration. Since sodium hydroxide is assumed to make up the total alkaline content, any other acids or bases will interfere. Although this method is not specific for sodium hydroxide, it is simple and requires little specialized equipment.

11.2 Qualitative Method for the Detection of Sodium Hydroxide in Air

The flame test is a fast way to determine if sodium ion is present. A flame will burn with an intense yellow colour when sodium ion is present (Moeller 1958).

Alkalinity, due to sodium hydroxide, may be determined qualitatively in the absorbing solution used in Section 11.1.1 above, with the use of pH paper.

11.3 Quantitative Methods for the Detection of Sodium Hydroxide in Water

11.3.1 Titration (ASTM 1979). This method may be used for concentrations of sodium hydroxide between 8 and 350 ppm in water when a 100 mL aliquot is titrated with 0.02 N hydrochloric acid. The range may be extended by changing the aliquot size or the concentration of acid titrant.

A representative sample is collected and stored in either a borosilicate glass or a polyethylene container. A suitable aliquot is taken and diluted as required. The aliquot used should contain not more than 15 mg of sodium hydroxide. Excess strontium chloride solution, 4.5 g/L, is added to precipitate dissolved carbonates and phosphates. The sample is boiled and allowed to cool. It is titrated using 0.02 N hydrochloric acid, with phenolphthalein as the indicator. Aluminates and chromates interfere. Since this method determines total alkalinity, other acid-consuming components will interfere. This is a fast, simple method requiring little specialized equipment.

11.3.2 Flame Photometry (AWWA 1976). This method may be used to determine sodium hydroxide present at concentrations above 0.02 ppm in water. This method is used when the sample contains high concentrations of acid-consuming components which interfere with a determination of total alkalinity. Sodium ion is determined using a flame photometer.

A representative sample is collected and stored in plastic bottles. A measured volume of the sample is filtered and diluted if necessary. Standard lithium solution is added as an internal standard. The sample is sprayed into a gas flame at 589 nm. A standard curve is used. High concentrations of calcium, magnesium, potassium, chloride, sulphate and bicarbonate interfere with the determination.

11.4 Qualitative Method for the Detection of Sodium Hydroxide in Water

High concentrations of sodium hydroxide in water may be detected with pH paper, but this test is not specific for sodium hydroxide. The flame test is a fast way to determine if sodium ion is present. Sodium causes a flame to burn with an intense yellow colour (Moeller 1958).

11.5 Quantitative Method for the Detection of Sodium Hydroxide in Soil

11.5.1 Flame Photometry

(Hesse 1972). Soils containing more than 0.4 ppm sodium hydroxide may be analyzed by this method. Sodium is determined in soil extracts using flame photometry.

A representative sample of 2 mm soil weighing approximately 5 g, accurately weighed, is placed in a 50 mL centrifuge tube and 30 mL of 0.5 M magnesium acetate solution are added. The tube is stoppered and shaken for 5 minutes, then centrifuged for 5 minutes at 400 rev/s until the supernatant liquid is clear. The supernatant is decanted into a 100 mL volumetric flask. The extraction is repeated twice more and the combined extracts are diluted to 100 mL. The sodium is measured using a flame photometer at 589 nm. High concentrations of calcium, magnesium, potassium, chloride, sulphate and bicarbonate interfere with the determination. Since this method measures sodium ion rather than acid-consuming components, it should be used with caution for samples taken from the sea coast.

11.6 Qualitative Method for the Detection of Sodium Hydroxide in Soil

High concentrations of sodium hydroxide in soil may be detected with the use of pH paper but the buffering capacity of the soil may suppress any change in pH. A better method for detecting sodium hydroxide is the flame test (Moeller 1958). An extract of the soil will impart an intense yellow colour to a flame if sodium ion is present.

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Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC$_{50}$	lethal concentration fifty
LC$_{LO}$	lethal concentration low
LD$_{50}$	lethal dose fifty
LD$_{LO}$	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P$_c$	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P$_s$	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T$_c$	critical temperature
TC$_{LO}$	toxic concentration low
Td	decomposition temperature
TD$_{LO}$	toxic dose low
TL$_m$	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight